CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter gives a brief description of the experimental techniques that have been utilized for the synthesis of silver-soda glass nanocomposites, followed by a description of various characterization techniques that have been employed to study the different properties of these resulting nanocomposites. Details of materials used in present study are discussed in section 2.1. The procedure of sample preparation is discussed in section 2.2. Physical vacuum deposition and ion-exchange techniques, used for the synthesis of silver-soda glass nanocomposites in the present research work are discussed in section 2.3 and 2.4 respectively. The optical properties of the synthesized nanocomposites have been characterized by UV-Visible spectroscopy which is discussed in section 2.5.1. The structural properties of prepared nanocomposites have been studied using Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) which have been described in sections 2.5.2 and 2.5.3 respectively. Section 2.5.4 describes photoluminescence study of synthesized nanocomposites. Surface hardness measurements of silver-soda glass nanocomposite samples carried out using Knoop microhardness technique have been depicted in section 2.5.5. The electrical properties of nanocomposites have been studied by I-V measurement technique as discussed in section 2.5.6.

2.1 Materials used in the Present Research Work

For the present research work, 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 demand for glasses with improved and varying combinations of surface properties is increasing day by day and so do the need for superior methods of fabricating such glasses. Reasons for choosing soda glass as a host matrix for embedding silver nanoparticles has been discussed under section 1.3 in chapter 1. The structure of soda glass has been discussed under section 1.3 in chapter 1. The softening point and annealing point of soda glass is 715°C and 548°C respectively. It has a refractive index of 1.515 [1].

For the synthesis of silver-soda glass nanocomposite samples by vacuum deposition technique, silver wire (purity, 99.9%) was used to make a thin film of silver on a glass substrate and was purchased from the local market. For ion-exchange process, silver nitrate (AgNO₃) and sodium nitrate (NaNO₃) were purchased from Rankem. Extra-pure acetone (99.5% purity) was procured from HiMedia Laboratories Pvt. Ltd., Mumbai, India. All chemicals were used as received.

2.2 Sample Preparation

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.

Physical vacuum deposition technique and ion-exchange technique were utilized to incorporate silver in soda glass matrix. Section 2.3 and 2.4 discuss in detail these techniques.

2.3 Physical Vapour Deposition Technique

Physical vapour deposition (PVD) is one of numerous physical thin film deposition techniques for the formation of nanocomposites in which metal nanoparticles and matrix are kept in the same environment. Deposition of thin films by PVD technique has widespread applications in many industrial sectors for example, metal-working industry, biomedical industry, automotive and aerospace industry [2-6]. Historically the first evaporated thin films were probably prepared by Faraday [7] in 1857 when he exploded metal wires in a vacuum. The deposition of thin metal films in vacuum by Joule heating was discovered in 1887 by Nahrwold [8] and was used by Kundt [9] in 1888 to measure refractive indices of such films.
There are primarily three physical vapour deposition processes, namely vacuum deposition, ion plating and sputtering. In the present work, vacuum deposition technique has been chosen to synthesize nanocomposite samples due to several advantages as discussed earlier in section 1.5.1 of chapter 1.

### 2.3.1 Vacuum Deposition by Thermal Evaporation

Vacuum deposition is a PVD process and is based on the thermal evaporation of the required material and its subsequent condensation on the substrate to be coated. The process is done in a high vacuum, as a result the atoms and molecules in the vapour phase do not collide with each other prior to arrival at the growth surface because the mean free path is very large as compared to the source to substrate distance [10].

**Mechanism of formation of Thin Film**

The steps in the growth of thin films are generally referred to as nucleation and growth. When a metal is heated, its atoms become more and more active. When the individual thermal velocities of these atoms become greater than the interatomic attraction forces of the metal atoms, they escape the parent metal and keep traveling at their original velocity so long as they do not collide with some other object. They get deposited on the first surface that they strike on. In nucleation, the atoms which are arriving at the surface lose thermal energy to the surface, and the surface absorbs that energy. Depending on the amount of thermal energy the atoms and the surface have, the atoms move about on the surface until they lose the thermal energy required to move about the surface and form nuclei. As nuclei continue to form, the film grows into a continuous sheet covering the entire substrate. The formation of clusters and their growth at the surface, depend mainly on the interaction energies of substrate atoms and atoms reaching the surface. The metal coating which condenses on the substrate possesses all the physical characteristics of the basic element. This property has greatly broadened the scope of application of the process [11-12].

### 2.3.2 Vacuum Deposition System

A schematic of the vacuum deposition system is shown in the Fig. 2.1. The vacuum deposition system consists of the following subsystems:

- Glass vacuum chamber
- Vacuum pumps (vapour diffusion pump backed up by rotary pump)
- Vacuum measurement gauges
- Water chiller unit
- Particle collection plate
- Crystal thickness monitor
- Tungsten filaments for melting the silver
- Power supply

**Figure 2.1:** Schematic of vacuum deposition system.
Figure 2.2: Photographic view of vacuum deposition system.

The vacuum deposition system has a cylindrical glass bell/SS jar chamber of diameter 300 mm and length 380 mm. The system has a vapour diffusion vacuum pump backed up by a rotary vacuum pump to evacuate the process chamber. The rotary pump, being capable of unassisted discharge to atmosphere is used initially to reduce the system pressure to about $10^{-2}$ to $10^{-3}$ Torr and then is used to back up the diffusion pump. The diffusion pump can reduce the pressure in the clean chamber to about $10^{-6}$ Torr. Pressure inside the process chamber was monitored with pirani and penning pressure measurement gauges. Water chiller provided cold water that was flown through the copper tubing coiled around the chamber of vapor diffusion pump. Tungsten filament was fixed to the electrodes which impart thermal velocity.
to the atoms of the parent metal and cause them to escape from the surface and follows a straight line path until they strike some cold surface. A base plate, circular in shape, hollow from inside was made up of stainless steel and has central pump in port which act as high vacuum valve. A quartz crystal film thickness monitor is mounted in the vacuum chamber. The vibration frequency of the crystal is proportional to the mass of material deposited on its surface. Calibrating this change in frequency to the atomic weight of the deposited material gives an accurate measure of the deposited film thickness.

For the present work, vacuum deposition system, depicted in Fig. 2.2, available in the Department of Physics, Kurukshetra University, Kurukshetra was used for depositing silver on soda glass samples.

**2.3.3 Synthesis of Silver-Soda Glass Nanocomposites by Vacuum Deposition followed by Annealing**

In the present work, thin films of silver were deposited on commercially available soda glass substrates by thermal evaporation using a “VEQCO” high vacuum evaporation unit EU-300 (Fig. 2.2) under a vacuum of the order of $10^{-5}$ Torr. All parts inside the glass vacuum chamber were cleaned with acetone or ethanol after fixing tungsten filaments. Prior to starting vacuum pumping, silver wire cuttings were kept in a tungsten filaments and glass substrate on which silver film was deposited placed at a substrate holder. Rotary vacuum pump was switched on to run for about 10-15 minutes to achieve pressure inside the process chamber of the order of $10^{-2}$ Torr, monitored by a pirani pressure measurement gauge. When the chamber pressure was in the range of $10^{-2}$ Torr, cold water supply to the vapour diffusion vacuum pump was started and diffusion vacuum pump was switched on. High vacuum valve of the process chamber was opened gradually and pressure inside the process chamber was measured by penning gauge. When the chamber pressure was in the range of $10^{-5}$ Torr, current to the filaments was gradually increased to achieve silver metal evaporation. After evaporation of silver metal, high vacuum valve was closed and the system was allowed to reach at the room temperature 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. The chamber was opened and silver deposited samples were collected.
Figure 2.3: Photographic view of furnace used for synthesis of nanocomposites.

Subsequently, silver deposited soda glass samples were annealed at various temperatures from 200°C to 550°C in air for 1 hour in furnace (Fig. 2.3) available in the Department of Physics, Kurukshetra University, Kurukshetra. After the heat treatment these samples were rinsed with concentrated HNO$_3$ solution to remove excess silver film adhering on the glass surface. Then, these silver deposited annealed samples were utilized for further characterization.

2.4 Ion-Exchange Technique

Ion-exchange is a widely used method for embedding metal nanoparticles in a soda glass matrix and has attracted increased attention as a suitable technique for fabricating optical glass waveguides, with application in integrated optics (telecommunications and sensor applications) to produce low-loss, fiber-compatible optical devices at low costs [13-18]. Glass strengthening by surface ion-exchange was the first industrial application of ion-exchange in glasses [14, 19-20] which emerged in the beginning of the 20th century. In this technique, large ion from an alkali salt melt (e.g. K$^+$) is exchanged with a smaller ion in the glass (e.g. Na$^+$), thus creating a compressive stress state at the glass surface. In 1918, Schott researchers observed that ion-exchange also produces a change in the refractive index of such a diffused layer. Thus, it is possible to modify mechanical, optical, electrical, chemical etc. properties of glass by ion-exchange process [21]. Ion-exchange in glass is typically carried out by replacing monovalent alkali ions present in a surface
layer of a glass substrate with different ions from a molten salt bath. In this method, the host matrix is dipped in a molten bath of a metallic compound at an elevated temperature, then ion-exchange occurs and the metallic ions are incorporated into the host matrix.

![Illustration of the melt-glass interface](image)

**Figure 2.4**: Illustration of the melt-glass interface (here $A^+ = Na^+$). $B^+$ is the cation of the melt (e.g. $Ag^+$, $K^+$, ...) which will be exchanged with the cation in the glass.

The principle of this technique is simple in which an ion ($A^+$) associated with a solid glass matrix ($X^-$) is replaced by another ion ($B^+$) with the same valence in melt salt:

$$X^- A^+ + B^+ \rightleftharpoons X^- B^+ + A^+$$

Let a glass substrate with the network-modifying ion $A^+$ (e.g. $Na^+$) be immersed into a molten salt with a cation $B^+$ (e.g. $Ag^+$, $K^+$, $Tl^+$...) as shown in Fig. 2.4. Since a gradient exists in both ion concentrations, a diffusion process will take
place, being essentially driven by thermal agitation. Random collisions will therefore cause replacement of A\(^+\) ion by the B\(^+\) ion in the glass matrix, which gradually forms a thin layer close to the surface. The process terminates when the substrate is allowed to cool down to room temperature. The exchange temperature is usually slightly higher than the melting point of the salt. Excessive heating may in fact cause damage to the surface due to nitrate decomposition and thermal relaxation of glass [22].

2.4.1 Synthesis of Silver-Soda Glass Nanocomposites by Ion-Exchange followed by Annealing

Silver exchanged glass slides were prepared by immersing the preheated soda glass slides for 1 min in a molten salt bath of AgNO\(_3\) and NaNO\(_3\) (1:4 weight ratio) mixture at the temperature of 350°C. The metallic ions are driven into the glass due to the chemical potential gradient and replace alkali ions of the matrix that are released into the melt. The thickness of the glass substrate, time of the ion-exchange process, and weight concentration of AgNO\(_3\) in the melt determined the concentration and distribution of Ag\(^+\) ions in the glass. After inter-diffusion, the obtained silver exchanged soda glass samples were rinsed with distilled water to remove excess AgNO\(_3\) adhering on glass surface.

Subsequently, these silver ion-exchanged samples were annealed at various temperatures from 200°C to 550°C for 1 hour in the furnace depicted in Fig. 2.3. All these experiments were carried out in an oxidizing atmosphere. When silver ion-exchanged glasses are annealed in air, the metallic ions are reduced to metal atoms. At elevated temperatures these metallic atoms diffuse through the host matrix and subsequently form nuclei. These nuclei would further grow to form metal nanoparticles of various sizes in soda glass matrix during thermal annealing. The resulting silver ion-exchanged soda glass samples annealed at various temperatures were utilized for further characterization.

2.5 Characterization Techniques

The silver-soda glass nanocomposite samples prepared as discussed above were analyzed using different characterization techniques to study their surface morphology and optical, structural, electrical, mechanical properties. Different
characterization techniques with their working principle and specifications have been discussed in the following subsections.

2.5.1 UV-Visible Spectroscopy

UV-Visible absorption spectroscopy is the measurement of the attenuation of electromagnetic radiations when they pass through a sample and results in the transitions between the various electronic energy levels of the sample [23-24]. The beam intensity attenuation $dI$ after traversing a differential thickness $dx$ can be written as

$$dl = -\alpha dx$$

where $I$ is the light intensity at a distance $x$ into the medium and $\alpha$ accounts for the amount of reduction due to constitution of the material. In the case of negligible scattering, $\alpha$ is called the absorption coefficient of the material. Integration of above equation gives

$$I = I_o e^{-\alpha x}$$

which gives an exponential attenuation law relating the incoming light intensity $I_o$ to the thickness $x$. This law is known as the Lambert-Beer law. Solving this equation we can get the relation between absorption coefficient and optical density (OD) ($\log I_o/I$).

$$\alpha = (OD)/(x \log e) = 2.303 (OD)/x$$

In the absorption mode, instrument itself converts the values of transmittance ($T$) into absorbance ($A$) by the relations given below.

$$T = I/I_o$$

$$A = 1 - I/I_o$$

$$T = 10^{-OD}$$

$$A = 1 - 10^{-OD}$$

In fact for low optical densities (O.D.), the above expression becomes $A \approx 1-(1-O.D.)=O.D.$, so that the absorption spectrum ($A$ versus $\lambda$ or $1-T$ versus $\lambda$) displays the same shape as the optical density. However, for high optical densities, typically higher than 0.2, the absorption spectrum gives a quite different shape to that of the
actual absorption spectrum \((\alpha \text{ versus } \lambda \text{ or O.D. versus } \lambda)\). After getting the O.D. from the instrument the values of absorption coefficient \('\alpha'\) can be calculated using equation (3). These values can be further utilized to determine optical constants of the material used.

As a part of thesis work, spectrophotometer (Shimadzu UV-2550PC) as shown in Fig. 2.5 was used for optical characterization of silver-soda glass nanocomposite samples.

![Figure 2.5](image)

**Figure 2.5:** UV-Visible Spectrophotometer (Shimadzu 2550PC).

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. All the absorption spectra were recorded keeping air as a reference whereas for recording diffuse reflectance spectra, BaSO₄ powder was taken as the reference material.

Fig. 2.6 shows the optical schematics of the UV-Visible spectrophotometer used in the present study. It consists of a light source, a holder for the sample, a monochromator to separate the different wavelengths of light and a detector. A single source covering the full UV-Visible wavelength range cannot be made accessible and so a combination of two independent sources are used - a deuterium
lamp for UV region and a tungsten/halogen lamp for visible region of the electromagnetic spectrum. The light source is switched automatically depending upon the wavelength used. The light emitted from the light source (deuterium lamp, D₂, or a halogen lamp W1) is reflected by the mirrors M1 and M2 and pass through a monochromator. This monochromator is a double monochromator of grating-to-grating type which is composed of the first monochromator (pre-monochromator) and the second monochromator (main monochromator). Electromagnetic radiations are first projected onto the pre-monochromator. The pre-monochromator is composed of S1 (entrance slit), M3 (mirror), G1 (grating), and S2 (exit slit). After passing through the pre-monochromator the light is projected onto the main monochromator. The main monochromator is composed of S2 (entrance slit), M4 (mirror), G2 (grating), M5 (mirror) and S3 (exit slit).

Figure 2.6: Optical schematics of UV-Visible Spectrophotometer (UV-2550).
After passing through S3, the light falls onto the beam chopper (CH). The beam chopper splits the light beams into the sample beam and reference beam. Light passing through the sample is measured by a detector, which is a photomultiplier (PM) tube which records the intensity of transmitted light, thus providing the transmittance as a function of wavelength. The UV-Visible absorption, transmission and reflection spectra of all the samples were recorded and numerical data were plotted in the “Origin 6.1”.

In order to operate the UV-Visible spectrophotometer in reflection mode, the incident light is allowed to fall on the sample and is recorded by the detector after multiple reflections with fully reflective inner surface of the sphere. The integrated spheres can be incorporated as additional instrumentation into conventional spectrophotometers [23]. The block diagram for such an arrangement is as shown in Fig. 2.7. The signal from the detector is recorded in computer where the data can be handled and presented using special software.

**Figure 2.7:** Schematic diagram for recording reflection spectra.

The absorption, transmission and reflection behaviour of materials towards incident light can be easily studied using UV-Visible spectroscopic technique. This technique provides a complete spectrum of the optical behaviour of material. It can give spectrum in all the three (absorption, transmission and reflection) modes. In the reflection mode, instrument itself measures the % reflection. By recording the absorption and reflection spectra using this technique one can easily calculate the
value of refractive index and dielectric constant of studied samples using the relation given under the section 1.6.1 in the chapter 1.

UV-Visible analysis can also give information about metal nanoparticles dispersed in a solvent or embedded in the insulator matrix. In such cases, absorption of incident radiations takes place due to surface plasmon resonance (SPR) of the metal nanoparticles as discussed in section 1.2.3 of chapter 1. Surface plasmons are essentially the light waves that are trapped on the surface because of their interaction with the free electrons of the metal [25]. When metal nanoparticles are embedded in dielectric media and specimen are exposed to the electromagnetic radiation, SPR absorption band is observed at a specific wavelength depending upon the nature of metal, matrix, size of the particles and distribution.

Let us consider an isolated spherical nanoparticle of radius R characterized by the size dependent dielectric function, \( \varepsilon \) (\( \omega \), 2R) and embedded in a dielectric matrix with a real dielectric function, \( \varepsilon_m \) as depicted in Fig. 1.4(a) in section 1.2.3 of chapter 1. This nanoparticle is immersed in the electric field \( E \) of a plane electromagnetic wave of frequency \( \omega \), and wavelength \( \lambda \gg 2R \). In this case it is assumed that an instant \( t \), the electromagnetic field is uniform. Thus, quasi static approximation (only the term dipolar electric is considered in the determination of the optical response) is considered. Under these conditions, the electric field inside the sphere is given by the Clausius Mossotti formula:

\[
E_t = \frac{3 \varepsilon_m}{\varepsilon(\omega) + 2 \varepsilon_m}
\]  

(8)

In the medium surrounding the nanoparticle, the electromagnetic field is the sum of the applied field and the field generated by a dipole located at the center of the nanoparticle. The dipolar moment is given by

\[
P = 3 \varepsilon \varepsilon_m \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} E
\]

(9)

where \( V \) is the volume of the nanoparticle. The polarizability \( \alpha(\omega) \) of a dipole immersed in a dielectric medium of dielectric function \( \varepsilon_m \) in the presence of a field \( E \) of frequency \( \omega \), is defined by the relation:

\[
P = \varepsilon \varepsilon_m \alpha(\omega) E
\]

(10)
Then, from above equations (9) & (10), the polarizability can be written as:

$$\alpha(\omega) = 3V \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

(11)

The absorption cross section is related to the polarizability by:

$$\sigma_{abs} = \frac{\omega\sqrt{\varepsilon_m}}{c} \text{Im}[\alpha(\omega)]$$

(12)

where $\text{Im}[\alpha(\omega)]$ is the imaginary part of the nanoparticle polarizability, $c$ is the light velocity in vacuum. Thus, from equations (11) and (12) we can deduce the expression of the absorption cross section:

$$\sigma_{abs}(\omega) = \frac{9\omega V\varepsilon_m^{3/2}\varepsilon_2(\omega)}{c[(\varepsilon_1(\omega) + 2\varepsilon_m)^2 + \varepsilon_2(\omega)^2]}$$

(13)

where $V$ is the particle volume, $\omega$ is the angular frequency of the exciting light, $c$ is the velocity of light, $\varepsilon_m$ is the dielectric constant of the host matrix and $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the frequency dependent dielectric constant of the nanoparticle. The SPR maximum occurs at resonance condition when $\varepsilon_1(\omega_{SPR}) = -2\varepsilon_m$ [26-29], where $\omega_{SPR}$ is the frequency of the SP resonance. At $\omega_{SPR}$, the metal nanoparticle interacts very strongly with the light, resulting in the collective coherent oscillations of the conduction electrons (with respect to the positive metallic lattice) in resonance with the electromagnetic field of the light. These oscillations bring the resonance known as the SPR in cross-section given by equation (4) at $\omega_{SPR}$ and this frequency is known as SPR frequency. The surface plasmon resonance frequency depends on the dielectric function as well as the metal particles size because $\omega_{SPR}$ is given by

$$\omega_{SPR} = \omega_p/\sqrt{\varepsilon_1(\omega_{SPR}) + 2\varepsilon_m}$$

which is directly proportional to the number of conduction band electrons $n_e$ through the equation

$$\omega_p^2 = \frac{4\pi n_e e^2}{m}$$

where $e$ is the electronic charge, $m$ is the electronic mass and $\omega_p$ is the plasma frequency of the metal.

### 2.5.2 Transmission Electron Microscopy (TEM)

Electron microscopy is a powerful method to investigate the internal microstructure of ultra thin specimen. TEM has high magnification ranging from 50 to $10^6$ and provide both image and diffraction information from a single sample [30].
A thin sample fixed on the grid is illuminated by an electron beam to perform analysis by TEM. Electron beam is partially transmitted through the sample, while part of it is scattered either elastically or inelastically. The elastically scattered electrons have undergone diffractions from the atomic planes of crystal whereas inelastic electrons arise from the phonon, plasmon and X-ray excitation. These electrons contribute towards formation of a diffuse halo around the transmitted beam, the diffracted beam and to the general background intensity between the diffraction spots. Most of the intensity at the exit surface of the crystal is in the transmitted and diffracted beam. In the bright field imaging mode, electrons transmitted through the sample are used to form image while intensity of scattered electron is filtered out [31].

The high magnification or resolution of TEM is a result of the small effective electron wavelength ($\lambda$) which is given by the de Broglie relationship [32]:

$$\lambda = \frac{h}{2m_qV^{1/2}}$$  \hspace{1cm} (14)

where $m$ and $q$ are the electron mass and charge, $h$ is Planck’s constant and $V$ is the potential difference through which electrons are accelerated.

The basic TEM instrumentation is summarized in Fig. 2.8. The main part of the illumination system is the electron gun which typically uses a LaB$_6$ thermionic emission source or a field emission source. The accelerating voltage is typically 60-300 kV. Electron microscopes have four types of lenses: condenser lenses, the objective lens, intermediate lenses and projection lenses. The condenser lenses are critically important for making a fine electron probe, while the objective lens determines the limit of image resolution. The first condenser (C1) controls the demagnification of the crossover (the spot size), whilst the second condenser (C2) controls the size and convergence of the probe at the specimen and hence the area of the sample that is illuminated. The specimen must not be more than a few hundred nanometers in thickness and is usually in the form of a 3 mm diameter disc. The specimen is located between the pole pieces of the objective lens. The combination of the objective lens and the projector lens system provides an overall magnification of around $10^6$. The selected area diffraction (SAD) aperture allows selection of a minimum sample area of ~0.1 µm diameter for electron diffraction. Smaller areas (down to a few nanometers in diameter) can be selected using a focused probe rather than an aperture; this is convergent beam electron diffraction (CBED).
Figure 2.8: Schematic diagram of the layout of a Transmission Electron Microscope.
In the present work, TEM measurements were performed using a Hitachi “H-7500” transmission electron microscope (Fig. 2.9) available at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh operated at accelerating voltage of 80 kV in order to determine the size of the silver nanoparticles embedded in soda glass matrix. For this study, samples were prepared in the following way: a diamond scribe was utilized to scratch the surface (a few microns below) of the glass containing silver nanoparticles. Minute powder thus obtained was carefully dropped in the methanol and kept for ultrasonification. Consequently, larger glass particles settled down and the finer ones floated on the surface of the liquid. The finest layer on the surface was collected on the carbon coated copper grid to view transmission electron micrograph. This instrument has a resolution of 0.36 nm with 40-120 kV operating voltage and can magnify object up to 6 lakh times in high resolution mode.

**Figure 2.9:** Transmission Electron Microscope, Hitachi “H-7500”.

2.5.3 Scanning Electron Microscopy (SEM)

SEM is one of the most widely used techniques for surface characterization of nanostructure materials. SEM is capable of producing high resolution images of sample surface. A stream of highly energetic, monochromatic electrons is focused on the sample. The incident beam is rastered across the sample surface to produce an image. As the electrons strike and penetrate the surface, a number of interactions occur that result in the emission of electrons and X-rays from the sample. The detectors collect these X-rays, backscattered electrons and secondary electrons and convert them into a signal that is sent to a screen, which produces the final image. When a high energy primary electron interacts with an atom, it undergoes either inelastic scattering with atomic electrons or elastic scattering with the atomic nucleus. In an inelastic collision with an electron, the primary electron transfers part of its energy to the other electron. When the energy transferred is large enough, the other electron will emit from the sample referred to as a secondary electron. Backscattered electrons are the high energy electrons that are elastically scattered and essentially possess the same energy as the incident or primary electrons. The probability of backscattering increases with the atomic number of the sample material [33].

The basic layout of SEM instrumentation is shown in Fig. 2.10. The SEM column consists of an electron gun, two condenser lenses, an objective lens, an electron detection system and a set of deflectors, all operating in a vacuum. In SEM electrons are thermionically emitted from tungsten or lanthanum hexa-boride (LaB$_6$) cathode filament towards an anode, alternatively electrons can be emitted via field emission. The electron beam which typically has an energy range from a few keV to 50 keV, is focused by two successive condenser lenses into a beam of very fine spot size (~5 nm). The beam then passes through the objective lens, where pairs of scanning coils deflect the beam either linearly or in a raster fashion over a sample surface; meanwhile, an appropriate detector monitors the secondary electrons or other signal such as backscattered electrons or X-rays, as they are emitted from each point on the surface. Simultaneously, using the same scan generator, a beam is scanned across the recording monitor. SEM mostly uses a PC to control the electron beam, to select the signals and to record as well as to store the digital images [34]. Microscopes using field emission guns are known as Field Emission Scanning
Electron Microscope (FE-SEM). Emitter type is the main difference between SEM and FE-SEM. Thermionic sources have relative low brightness, evaporation of cathode material and thermal drift during operation. Field emission is one way of generating electrons that avoid these problems. FE-SEM uses field emission source producing a cleaner image, less electrostatic distortions and spatial resolution < 2nm (that means 3 or 6 times better than SEM).

Figure 2.10: Schematic diagram of the layout of a Scanning Electron Microscope.

Energy Dispersive Analysis of X-rays (EDAX)

Compositional analysis of the samples was carried out by the energy dispersive X-ray spectroscopy attached with the SEM. This is one of the versatile accessories of scanning electron microscopes for determining the chemical composition of unknown materials. During EDAX analysis, a high-energy electron beam hits a specimen, X-rays characteristic of the atoms in the specimen are generated. The incident electron beam may knock out an electron from the inner shell and a vacancy is created in the inner shell. An electron from an outer, higher-
energy shell then fills this vacancy and the difference in energy between the higher-energy shell and the lower-energy shell is emanated in the form of X-rays. The intensity and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. Each atom emits its own characteristic X-rays. Thus, by measuring the energy of the X-rays being released by a specimen during electron beam bombardment the identity of the atom from which the X-rays was emitted can be known and by measuring intensity of X-rays, corresponding concentration of each element can be deduced [33].

Figure 2.11: FE-SEM Quanta 200FEG.

In the present work, morphology of the silver-soda glass nanocomposite samples synthesized using vacuum deposition technique was studied using FE-SEM Quanta 200FEG (Fig. 2.11) available at Institute Instrumentation Centre, IIT Roorkee. Silver-soda glass nanocomposite sample was coated with a very thin layer of gold by sputtering technique. The coated sample was then subjected to SEM studies. SEM measurements of nanocomposite samples synthesized by ion-exchange technique were carried out using LEO 435 VP scanning electron microscope available at Department of Physics and Chemistry, University of Southern Denmark, Denmark.
2.5.4 Photoluminescence (PL) Study

Photoluminescence is the spontaneous emission of light from a material under optical excitation. It is a process in which a material absorbs UV radiations and then emits a part of it at a different wavelength in visible region. In this process only a part of absorbed energy is transformed into light energy and the rest of it ends up in form of heat [35].

PL in solids can be classified according to the nature of electronic transitions producing the luminescence. In PL, a molecule absorbs light of wavelength $\lambda_1$ decays to lower energy excited electronic state and then emits light of wavelength $\lambda_2$ as it radiatively decays to its ground electronic state. Luminescence can be either fluorescence or phosphorescence depending upon the average life time of excited state. The basic principle for fluorescence spectroscopy can be realized by Jablonski’s diagram (Fig. 2.12) which shows that the fluorescent state of a molecular entity is the lowest excited state from which the transition to the ground state is allowed, whereas the phosphorescent state is metastable state below the fluorescent state, which is reached by radiationless transition. In the most typical cases, the fluorescent state is the lowest singlet excited state and phosphorescent state is the lowest triplet state, the ground state being a singlet. Presently, modified Jablonski’s diagram are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines, displaced vertically to indicate relative energies, are grouped according to multiplicity into horizontally displaced columns. Excitation and relaxation processes that interconvert states are shown in the diagram by arrows. Radiation transitions are generally indicated with straight arrows, while radiationless transitions are generally indicated with wavy arrows.

The PL spectrum is obtained by plotting the relationship between the wavelength and the intensity of the emitted light from a sample excited by an appropriate excitation source of constant energy. The excitation source can be light, an electron beam, heat, X-rays or radiation from radioactive materials. The spectrum is obtained using a monochromator equipped with an appropriate light detector. In the case of an excitation spectrum, on the other hand, the relationship is obtained by observing changes in the emitted light intensity at a set wavelength while varying the excitation energy. When the excitation source is light, single-frequency light
produced by a monochromator impinges on the sample and the emitted light intensity is recorded as the excitation wavelength is varied. The excitation spectrum gives information on the positions of excited states, just as the absorption spectrum does, except that the former reveals only absorption bands that result in the emission of light. The observed difference between the absorption and excitation spectra can yield useful information. In a spectrum, light intensity at a given wavelength is expressed along the ordinate and the wavelength along the abscissa.

![Diagram](image)

**Figure 2.12:** Jablonski’s diagram illustrating the processes involved in the creation of an excited electronic singlet state by optical absorption and subsequent emission via the singlet, $S_1$, (fluorescence) or the triplet state, $T$, (phosphorescence).

A spectrofluorometer is an analytical instrument used to measure and record the fluorescence of a sample. While recording the fluorescence, the excitation, the emission or both wavelengths may be scanned. The apparatus for measuring the spectral characteristics of nanocomposite samples is shown in Fig. 2.13. The excitation source consists of the light source and a monochromator, which selects a specific wavelength range from the incoming light. (The monochromator can be replaced by a filter). The light emitted from the sample is analyzed by a monochromator equipped with a light detector. The light detector transforms the photons into electrical signals. After the signals are amplified, they are recorded.
with photomultiplier tube. It is often convenient to collect all spectral data in the form of digitized electrical signals and to use a computer for further processing the data.

![PL measurement apparatus](image)

**Figure 2.13:** PL measurement apparatus.

A photographic view of this spectrometer (FlouroMax®-3) used in the present study is shown in Fig. 2.14. This facility is available in our own department. The FlouroMax®-3 contains Czerny-Turner monochromators for excitation and emission. The Czerny-Turner design uses all reflective optics to maintain high resolution. The brief description of FlouroMax®-3 is as follows [36]:

**Gratings**

The essential part of a monochromator is a reflection grating. A grating disperses the incident light by means of its vertical grooves. A spectrum is obtained by rotating the grating and recording the intensity values at each wavelength. The gratings in the FlouroMax®-3 contain 1200 grooves per mm and are blazed at 330 nm (excitation) and 500 nm (emission). Blazing is etching the grooves at a particular angle, to optimize the grating’s reflectivity in a particular spectral region. The wavelengths selected are optimal for excitation in the UV and visible region and for emission in the higher-UV to near-IR. Each grating is coated with MgF₂ for
protection against oxidation. The system uses a direct drive for each grating, to scan the spectrum up to 200 nm s^{-1}, with accuracy better than 0.5 nm and repeatability of 0.3 nm.

**Figure 2.14:** Spectrofluoremeter FlouroMax®-3.

**Slits**

The entrance and exit ports of each monochromator have continuously adjustable slits controlled by Datamax (software package available with FlouroMax-3). The width of the slits on the excitation monochromator determines the bandpass of light incident on the sample. The emission monochromator’s slits control the intensity of the fluorescence signal recorded by the signal detector. When setting slit width, the trade-off occurs between the intensity of signal and spectral resolution. The wider the slits are, the more light falls on the sample and detector, but the resolution decreases. The narrower the slits are, the higher the resolution gets, but at the expense of signal.

**2.5.5 Surface Hardness Analysis**

Hardness is one of the important characteristic property of materials which enables to resist permanent penetration, indentation and scratching. The principal purpose of the hardness test is to determine the suitability of a material for a given
application, or the particular treatment to which the material has been subjected. Generally, the hardness of the materials is determined by means of indentation based hardness testing. Hardness testing can be divided into two groups: in macrohardness testing the load applied to test the material is larger and is in order of one kilogram or more while in microhardness testing the load applied to test the material is very low i.e. below one kilogram [37]. Normally, the surface hardness studies are preferred at very low loads even below 10 grams.

2.5.5.1 Knoop Microhardness Test

The Knoop microhardness test is particularly used for very brittle materials such as glasses or thin specimens, where only a small indentation may be made for testing purposes. This test method was developed in 1939 by F. Knoop and colleagues at the National Bureau of Standards in the United States. In Knoop hardness testing, a pyramidal diamond indenter is pressed into the surface of the test material after selecting the required test force, for a specified dwell time. The indenter is removed after the dwell time. The indenter produces an elongated diamond shaped image on the surface of the sample. The size of the indenter on the surface of the sample is measured using high resolution optical microscope. The geometry of this indenter is an extended pyramid with the length-to- width ratio of about 7:1 and respective face angles are 172°-30' for the long edge and 130° for the short edge. The hardness of the material is determined by the depth to which the Knoop indenter penetrates. The depth of indentation is about 1/30 of the long diagonal length. The advantages of the test are that only a very small sample of material is required, and that it is valid for a wide range of test forces [38-39].

Knoop microhardness number is defined as the ratio of the indentation load to the indentation area of the resultant indentation impression. The Knoop microhardness number (KHN) is given by the formula

\[
KHN = \frac{load \ (kgf)}{indentation \ area \ (mm^2)} = \frac{P}{C_p d^2}
\]  

(15)

where \( P \) = applied indentation test load, \( d \) = length of indentation along its long diagonal and \( C_p \) = correction factor related to the shape of the indenter, ideally 0.070279. Fig. 2.15 illustrates the Knoop indenter and the indentation produced.
Figure 2.15: Knoop indenter and the indentation produced.

Figure 2.16: UHL microhardness tester.
In the present work, Knoop microhardness measurements of the prepared silver-soda glass nanocomposite samples were carried out at room temperature using Knoop indentation technique with a UHL microhardness tester as shown in Fig. 2.16 available at the department of Physics, Kurukshetra University, Kurukshetra. Test load from 9.8 to 490.33 mN were applied for a dwell time of 30 sec. In this method to minimize the measurement errors, at least ten indentations were made at each test load. The mean value of KHN was calculated along with its standard deviation.

### 2.5.6 Electrical Conductivity Behaviour

Analyzing the current-voltage (I-V) relationship gives an indication whether the nanocomposite conductivity is due to tunneling or direct contact between the particles. Linear I-V relationship i.e. ohm’s law, indicates that direct contact between the filler particles is the dominant conduction mechanism. However, tunneling mechanism is the dominant mechanism for composites characterized by power law I-V relations such as Fowler-Nordheim (FN), Richardson-Schottky (RS) and Poole-Frenkel (PF) emission processes, as well as the Space Charge Limited Current (SCLC) conduction process. In the present work, conduction mechanism analysis was done by applying established transport models for the description of carrier transport in semiconductor metal as well as dielectric systems to I–V data [40-41].

![Scheme of Experimental Setup](image)

**Figure 2.17:** Scheme of Experimental Setup.
In the present study, DC Current-Voltage (I-V) measurements of silver-soda glass nanocomposite samples were performed on Keithley Digital Electrometer 6517A at room temperature with computer interface assembled with a two probe arrangement as shown in Fig. 2.17 available at the department of Physics, Kurukshetra University, Kurukshetra.

![Keithley Digital Electrometer 6517A](image)

**Figure 2.18:** Keithley Digital Electrometer 6517A.

A photographic view of this Keithley Digital Electrometer 6517A is shown in Fig. 2.18. This electrometer (6517A) has an in-built capability of output independent voltage source of ±1000V. So, the same equipment (6517A) was used to apply the voltage across the sample and to measure the current through the sample. It has two spring load contact probes. These probes move in a pipe and are insulated by Teflon washers. This probe arrangement is mounted in suitable stand, which also holds the sample plate. The sample was laid between the two electrodes. A testing voltage 10 volt was applied. The current passing through the sample was determined by the pico-ammeter and resistance of the sample could be calculated.
References


