CHAPTER 1

INTRODUCTION

Glass has fascinated mankind from thousands of years as it possess several desirable properties which make it an interesting material [1-2]. However, its usage has always been limited due to its unwanted properties such as low tensile strength, resistance against fracture, low hardness etc. Recently, formation of composite materials by incorporation of metal nanoparticles in glass matrices has attracted increasing attention as they exhibit striking optical, electrical, thermal effects that make them promising candidate for various nanotechnological applications [3-8]. The remarkable modifications in properties displayed by these nanocomposites depend on the amount, size and shape of embedded nanoparticles [9-10].

To realize metal doped glass nanocomposites a number of techniques such as low energy ion beam mixing [11], sol-gel [12], direct metal-ion implantation [13], ion-exchange [14-15], vacuum deposition [16], field-assisted ion diffusion [17] etc. have been utilized. In most of these techniques dopants are first introduced into the glass matrix and then the doped glasses are treated by proper combination of treatments such as irradiation by either low-mass ion beams or electrons, heat treatment in reducing atmosphere or pulsed laser irradiation [18]. Such post-treatments aggregate the nanoparticles into nanometer sized clusters.

In the present research work, vacuum deposition and ion-exchange techniques followed by thermal annealing in air has been chosen to synthesize silver-soda glass nanocomposites. These methods are highly favorable as they are very efficient for introducing very high concentrations of metal ions into the glass matrix and simultaneously keeping it intact. Variations in optical, structural, mechanical and electrical properties of fabricated nanocomposites with annealing temperature have been investigated.
A brief outline about concept of nanomaterials with their classification is
described in section 1.1. Section 1.2 describes the concept of nanocomposites, their
classification and history of metal-glass nanocomposites. Selection of host matrix
with its basic structure is discussed in section 1.3. Section 1.4 contains the choice of
filler and its applications. Overview about the methods of synthesis of
nanocomposites is given in section 1.5. Section 1.6 describes the modified
properties of nanocomposites and related literature. Justification and aim of the
present work are described in the section 1.7.

1.1 Concept of Nanomaterials

Miniaturization is a general aim of all the research and technological
developments that are taking place to produce smaller, faster, lighter and cheaper
devices with greater functionality while using fewer raw materials and consuming
less energy. Research in the field of nanomaterials is a step towards miniaturization
of technology that will contribute significantly towards a sustainable usage of raw
material and energy [19]. The history of nanomaterials is quite long; however, major
developments within nanoscience have taken place during the last three decades.

The idea of nanotechnology was first highlighted by noble laureate Richard
Feynman, in his famous lecture at the California Institute of Technology on 29th
December, 1959 and he also discussed the idea of nanomaterials in one of his
articles titled, “There is plenty of room at the bottom”. He underlined that from this
nanoscale should arise new physical and chemical properties [20-21]. The term
nanoparticle, which represents another form of nanomaterials, came into frequent
use in the early 1990s by the materials science community to represent particles that
are composed of up to tens of thousands of atoms but confined to size less than 100
nm, until then, more general terms like submicron and ultra-fine particles were in
use.

One nanometer (abbreviated as 1 nm) is one billionth of a meter. To get a
sense of the nanoscale, a human hair measures 75,000 nm or 8-10 hydrogen atoms
lined up end to end make 1 nm [22]. Research in the field of nanoscience is a
multidisciplinary effort that involves interaction between researchers in the field of
physics, chemistry, materials science, mechanics and even biology and medicine
[23].
Nanomaterials are those materials that possess at least one characteristic dimension in nanoscale i.e. 1 to 100 nm. Nanomaterials exhibit many unique properties such as enhanced chemical reactivity, lowering of melting point, nonlinear optical behaviour, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behaviour and electric resistivity [24-26] etc. for which they are being extensively studied in various research fields. Researchers have proposed a huge range of potential scientific applications of nanomaterials in the fields of biotechnology, sensors, medical diagnostics, catalysis, high performance engineering materials, magnetic recording media, optics, conducting adhesives [27-28] etc. Two principal factors that are responsible for the alteration in properties of materials when they are reduced to nanoscale are increased surface to volume ratio resulting in a large number of surface atoms relative to the total number of atoms and quantum confinement effects [29]. For example, thermodynamic processes change at the nanoscale due to increase of surface energy as the size of the material decreases [29]. In addition, many nanomaterials act as catalysts as their high energy surfaces are more reactive than the surfaces of bulk material such as gold which is chemically inert at normal scale while act as a powerful chemical catalyst at nanoscale [30-31].

1.1.1 Classification of Nanomaterials

Based on the number of dimensions which lie within nanometer range, nanomaterials are usually classified into three classes (Fig. 1.1): (1) 1-Nano Dimensional Materials: The materials having one dimension in nanoscale are called 1-nano dimensional materials such as nanofilms, coatings, multilayers etc. (Fig. 1.1 a). (2) 2-Nano Dimensional Materials: The materials having two dimensions in nanoscale are called 2-nano dimensional materials such as carbon nanotubes, nanofibres, nanowires etc. (Fig. 1.1 b). (3) 3-Nano Dimensional Materials: The materials which have all the dimensions in nanoscale such as nanopowders, nanoparticles, nanocrystalline materials, quantum dots etc. are called 3-nano dimensional materials (Fig. 1.1 c) [32-33].

1.1.2 Properties of Nanomaterials

Nanomaterials exhibit many unique properties, for which they are intensely being studied in diverse research fields. Unlike bulk materials that have constant
physical properties regardless of mass, nanomaterials have unique size dependent properties. Indeed the possibility to control the properties, by tuning the size of the nanoparticle, has been the cause and subject of many investigations. One such example is that the reduction of material’s dimension has pronounced effects on its optical properties such as absorbance, luminescence, reflectivity, refractive index etc. For example, colloidal solutions of gold nanoparticles have a deep red colour which becomes progressively more yellow as the particle size increases. Mechanical properties (especially hardness and strength) are highly dependent on the presence of defects within a material. As the system size decreases, the ability to support such defects becomes increasingly more difficult and mechanical properties are altered accordingly. The properties of nanoparticles arise as a consequence of the huge fraction of surface atoms in the total amount of atoms and increasing influence of the wave-like property of electrons i.e. quantum mechanical effects [29] which have been explained briefly in the following section.

![Figure 1.1: Classification of Nanomaterials.](image)

### 1.1.2.1 Surface Area to Volume Ratio

Surface of nanomaterials plays an important role in determining their properties. Materials in nanosize have high surface area to volume ratio. If we assume that these nanoparticles are spherical having radius \( r \), the surface area to volume ratio of material is equal to

\[
\frac{S}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \tag{1}
\]
Therefore, \( S/V \alpha 1/r \) which implies that decreasing the particle radius increases the surface area to volume ratio. For example, for a cube of volume 1 cm\(^3\), the percentage of surface atoms will be only \(10^{-5}\%\). When the cube is divided into smaller cubes with an edge of 10 nm, the percentage of surface atoms will increase to 10\%. In a cube of 1 nm\(^3\), almost every atom will be a surface atom. Such a drastic increase in ratio of surface to volume atoms in nanomaterials is responsible for change in their physical and chemical properties. As the surface of the particle is involved in chemical reactions, large surface area can make materials more active [34].

### 1.1.2.2 Quantum Confinement Effects

In a bulk crystal, the properties of the material are independent of size and are dependent only on chemical composition. As the size of the crystal is reduced to the nanometer range, the electronic structure is altered from the continuous electronic bands to discrete or quantized electronic levels.

**Figure 1.2:** The variation of density of states \(g(E)\) with energy \((E)\) for the infinite bulk solid, a quantum film, a quantum wire and a quantum dot.
As a result, the continuous optical transitions between the electronic bands becomes discrete and the properties of the nanomaterials become size dependent [35-36]. The density of states changes as one goes from the bulk to quantum films that are confined in one dimension to quantum wires confined in two dimensions and finally, the quantum dots that are confined in all the three dimensions. The variation of density of states g(E) versus energy (E) is shown schematically in Fig.1.2. This variation of density of states versus energy for confined systems does not follow the typical $E^{-1/2}$ dependence, as in the case of an infinite solid.

Important among these nanoscale materials are nanocomposites, in which the constituents are mixed at nanometer length scale. They have unique properties that are different from their bulk counterparts. The study of nanocomposite materials requires a multidisciplinary approach involving novel synthesis techniques and an understanding of physics and surface science. Therefore, in depth studies related to nanocomposite materials is of immense significance both from fundamental as well as applied point of view.

1.2 Nanocomposites

Nanocomposites are composites containing different compositions or structures, where at least one of the constituent is in the nanoscale regime in other words nanocomposites are materials that are created by introducing nanomaterials (often referred to as filler) into a macroscopic sample material (often referred to as the matrix) [37-39]. After adding nanomaterials to the matrix material, the resulting nanocomposites not only exhibit enhanced electrical and thermal conductivities but also distinctive optical and dielectric properties due to their quantum size effects and surface effects. Nanocomposite materials are emerging as suitable alternatives to overcome limitations of micro composites. They are reported to be the materials of 21st century as they possess unique design and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached [40], even though the first inference on them was reported about thirty years back [41].

1.2.1 Classification of Nanocomposites

Nanocomposites can be classified according to their matrix materials into three different categories i.e. metal matrix nanocomposites, ceramic matrix
nanocomposites and polymer matrix nanocomposites. Nanocomposite of insulating materials such as glasses, ceramics or polymers with embedded metal nanoparticles are under focus because of their special structural, mechanical, electrical, linear and nonlinear optical properties.

Among the nanocomposites, metal-glass nanocomposite materials exhibit interesting novel properties which include nonlinear optical behaviour, increased mechanical strength, high refractive index, electrical resistivity etc. Such nanocomposites containing metal nanoparticles dispersed in glass matrices have also drawn attention because of their second order non-linear effects and have applications in developing high speed and low power optical devices for future communication systems [42-43]. Thus the aim of the present work was to synthesize silver-soda glass nanocomposites and to investigate structural, optical, mechanical and electrical properties of fabricated nanocomposites.

1.2.2 History of Metal-Glass Nanocomposites

Although nanoparticles are often considered as the innovation of modern technology, the use of metal nanoparticles for “artistic” applications is not new at all. In fact nanocomposites formed by incorporating transition metal nanoparticles in glass matrices display peculiar optical properties that have made them famous since literally the millennia. The first glasses containing metal nanoparticles were fabricated by Roman glassmakers in the fourth century AD. One example of this technology has been preserved till date in the form of *Lycurgus Cup* as shown in Fig. 1.3 [44-45]. This cup is made of a soda-lime glass containing very minute amount of silver and gold. This extraordinary cup is the only complete example of a very special type of glass, known as dichroic, which changes colour in the presence of light. The opaque green colour of the cup turns to a glowing translucent red when light is put inside it. This peculiar colour display is due to the presence of tiny amounts of colloidal gold and silver embedded inside the glass [46]. Medieval cathedral windows demonstrate great varieties of beautiful colours due to the nanosized metal particles embedded in the glass matrix. The first attempt to explain the nature of the colour induced in the glasses by metal nanoparticles can be attributed to Michael Faraday [47]. Since then, studies dedicated to the optical properties of metal-glass nanocomposites have been developing continuously.
Nonlinear optics has provided further motivation for the development of preparation and characterization methods for metal-glass nanocomposites.

Figure 1.3: Roman Lykurgos goblet (fourth century AD) made of soda-lime glass containing silver and gold particles. Colour changes from opaque green to strong red when the light source is put inside [44].

In 1905 Maxwell Garnett formulated the first theoretical approach for understanding the interaction of light with metal nanoparticles [48-49]. The Maxwell-Garnett articles discusses the optical properties of a medium containing metal nanoparticles, showing that the colors of metal nanoparticles could be explained using the theory developed by Lorentz in 1880 [50] for non-homogeneous optical systems. Gustav Mie observed that the Maxwell-Garnett explanation was not
suitable for the colours observed in different experimental conditions of dilute solutions with metal nanoparticles. Mie was able to explain it theoretically in 1908 by solving Maxwell’s equations [51-52]. He proposed that the interaction of light with metal nanoparticles can give rise to collective oscillations of the free electrons commonly known as surface plasmons.

1.2.3 Surface Plasmon Resonance

The surface plasmon resonance (SPR) is the coherent motion of the conduction band electrons caused by interaction with an electromagnetic field [3, 29, 53-56]. Fig. 1.4(a) depicts the systematic representation of interaction between an incoming electromagnetic field and metallic nanoparticles. In a classical description, the electric field of an incoming light wave induces polarization of electrons with respect to the much heavier ionic core of a spherical nanoparticle as shown in Fig. 1.4(a). As a result, net charge difference appears on the surface of the nanoparticle, which in turn acts as a restoring force. Consequently, this net charge difference oscillates with the incident electric field known as plasmon oscillation.

![Figure 1.4 (a): Schematic diagram illustrating the collective oscillations of free electrons under the effect of an electromagnetic wave.](image)
Thus the final properties of the resulting material can be easily control by taking care of these factors. Different metal nanoparticles produce different light interactions and therefore different colours. As an example, bulk gold looks yellowish in reflected light, while thin gold films look blue in transmission. This blue colour steadily changes to orange as the particle size is decreased to ~ 3 nm.

1.2.4 Metal-Glass Nanocomposites

Metal-glass nanocomposite is an exciting emerging area of research. The reasons for the present excitement in the metal-glass nanocomposite research are due to their several inherent advantages over other dielectric nanocomposites, exceptional properties, unique functions in nanoscience and future nanotechnology [42, 60].

Metal-glass nanocomposite is a class of materials in which metallic nanoparticles are embedded in a glass matrix in order to dramatically improve the properties of the glass as compared to their traditional bulk composites. At this scale large surface area of nanoparticles even at very low concentration can noticeably
change the macroscopic properties of the glass and contribute many new characteristics to the glass. Properties which have been shown to undergo substantial improvements include [7, 61-66]:

- Surface appearance (colour)
- Optical properties (refractive index)
- Linear and nonlinear optical behaviour
- Electrical conductivity
- Mechanical properties (surface hardness)
- Corrosion resistance

The incorporation of metal nanoparticles into the glass matrix allows the construction of devices to utilize their advantageous properties. The host matrix not only forms the structure of device but also protects the nanoparticles and prevents agglomeration. These nanocomposite materials have a huge range of potential scientific applications such as in the fields of optical data storage media, optical waveguides, optical switches based on their nonlinear optical properties, photochromatic and colour glass recycling industry, solid-state lasers, sensors, coloured glasses, dichroic polarizers, display devices, enhanced fluorescent materials, modified refractive index materials, solar cells, optoelectronic materials etc. [8, 43, 67-76]. In all these applications size, shape, number density and distribution of the nanoparticles critically determine performance and properties of the metal-glass nanocomposites.

1.3 Selection of Host Matrix: Soda Glass

Glass is an amorphous (non-crystalline) solid material that possesses no long-range atomic order. It is formed by fusion of mixture of silica, basic oxides and some other compounds and is solidified from the liquid state without crystallization [1-2].

A wide range of substances can form glasses, including covalent, ionic, metallic, van der wall and hydrogen bonded materials. These glass-forming oxides can be relegated into three types: network or glass formers, conditional glass-formers and network modifiers. The most important glass formers SiO₂ form glasses on their own when cooled from their molten state. However, the conditional glass-formers (e.g. BeO, ZnO, Al₂O₃, etc.) do not form a glass network on their own and
need to be melted along with a suitable oxide to form glass. These intermediate oxides have coordination numbers and bond strengths between the network-formers and network-modifiers. The network-modifiers (e.g. CaO, BaO, MgO, Na\textsubscript{2}O, K\textsubscript{2}O, Li\textsubscript{2}O etc.), having large coordination numbers and relatively weak bonds and they are distributed throughout the holes in the network. They alter the glass-forming network by replacing stronger bridging oxygen (BO) bonds with weaker, nonbridging oxygen (NBO) bonds. Especially, sodium ions depolymerize the silicon oxygen continuous random network by breaking the Si-O-Si bonds and randomly reside in the structural interstices thus created. These network modifiers are generally added to the glass to change its properties like softening point, fluidity, resistivity, thermal expansion coefficient, chemical durability etc. [77].

Figure 1.5: Two dimensional schematic representation of the random network of silicate glass [79].
As properties of glass depend upon its chemical composition and atomic structure, thus the understanding of their structure is important from a fundamental point of view.

Fig. 1.5 shows the structure of silicate glass. The basic structural unit of glass network is the silicon-oxygen tetrahedron in which a silicon atom is connected to oxygen atoms through each corner. The oxygen atoms shared between two tetrahedral are called bridging oxygen (BO). Those not shared are referred to as nonbridging oxygen (NBO). X-ray and neutron diffraction studies indicate that the Si-O distance in the tetrahedron is 1.61 Å and the shortest O-O distance is 2.65 Å, same as that of crystalline silica [78]. The inter-tetrahedral (Si-O-Si) bond angle distribution is centered at approximately 143°, which is much broader than that of crystalline silica; hence do not show long-range order, as shown schematically in Fig. 1.5. The lower density of pure silica can be attributed to the existence of defects and holes in the network. Ion-exchange in pure silica takes place through these defects and holes at relatively higher temperatures and applied electric field. The temperature to obtain pure silica is very high and thus makes it expensive.

When network-modifiers (alkali ions) are added to silicate glasses, they fill the gaps and holes existing therein by raising the concentration of nonbridging oxygens, which, in turn, lowers the connectivity of a structure. This decrease in the connectivity of SiO₄ tetrahedral network causes a subsequent decrease in the transition temperature and melts viscosity as well as an increase in thermal expansion coefficient, density and ionic conductivity. The resulting modified-random-network has alkali-rich regions surrounded by presilicate network. Since alkali ions exhibit lower density and higher mobility through interstices, they contribute much to the ionic conductivity. The concentration of alkali considerably changes the ionic and thermal properties of an oxide glass, and thus, this behavior is exploited in the realization of doping with foreign atoms for optical waveguide fabrication [80]. Soda glass is an important and widely used example of such glasses.

A typical composition of a soda glass is 69-74 wt% SiO₂ (silicon dioxide), 10-16 wt% Na₂O (Sodium Oxide) and 5-14 wt% CaO (calcium oxide) with much smaller amounts of various other compounds [81]. Network modifiers such as Na₂O and CaO are added to silica to alter the network structure by replacing Si-O-Si
bonds with Si-O' Na⁺ or Si-O' Ca²⁺ bonds. This separates the SiO₂ tetrahedral from each other, which makes the mixture more fluid and therefore more likely to form a glass after it has been melted and then cooled. The modified-random-network is shown schematically in Fig. 1.6. Small amounts of other compounds (Al₂O₃, MgO, CaO etc.) are added for tailoring other properties of glass such as durability, refractive index, expansion coefficient, melting point etc. It is the most common type of glass and is used in the construction industry.

Figure 1.6: Two dimensional schematic representation of modified-random-network of glass [79].
In order to increase applications of glass in various fields, glass materials are combined with the emergent field of nanotechnology via the incorporation of nanoparticles into glass to produce novel materials. The selection of suitable glass matrix for the synthesis of metal-glass nanocomposites by using the vacuum deposition and ion-exchange techniques play an important role in controlling the features of nanoparticles such as size, shape and distribution. Depending on the nature and possibility to utilize the structural network variety of glasses can be selected for incorporating various metal nanoparticles. The alkali content must be high enough (Na$^+$) to perform a suitable diffusion.

In the present study, we have chosen soda glass as a host matrix for embedding nanoparticles because they have a high Na$^+$ content and are easily available. Moreover, soda glass is transparent, inexpensive, chemically stable, reasonably hard and extremely workable. These exceptional properties of soda glass make them widely used engineering material [82-83]. Soda glass have wide spread applications in diverse disciplines such as photonic devices, optical sensors, biosensors, optical waveguides, light emitting diodes, integrated optics for communication as well as in many other optical components [84-90].

It is excellently suited as a matrix for fundamental research on nanocomposites as it involves minimal chemical interaction between the nanoparticles and the host matrix. Moreover, glass matrices provide long-term stability to metal nanoparticles. In glass even the smallest metal nanoparticles can be stabilized and investigated [91-92].

1.4 Choice of Filler

1.4.1 Silver (Ag) Nanoparticles

Recently metals with free electrons (essentially Au, Ag and Cu) are being investigated extensively as they exhibit plasmon resonances in the visible spectrum and have wide spread applications in diverse disciplines. Although silver and gold share many similar properties and applications, interestingly, gold nanoparticles have been exploited to a much larger extent than silver nanoparticles for potential applications despite the fact that silver nanoparticles exhibit higher efficiency of plasmon excitation which in turn leads to enhanced properties including catalysis [93], magnetic and optical polarizability [94], electrical conductivity [95] and
antimicrobial activity [96]. The reason for the considerable interest in the use of silver nanoparticles can best be summarized by quoting the following statement [97-98]:

Of the three metals (Ag, Au, Cu) that display plasmon resonances in the visible spectrum, silver exhibits the highest efficiency of plasmon excitation. Moreover, optical excitation of plasmon resonances in nanosized silver particles is the most efficient mechanism by which light interacts with matter. A single silver nanoparticle interacts with light more efficiently than a particle of the same dimension composed of any known organic or inorganic chromophore. The light interaction cross-section for silver can be about ten times that of the geometric cross section, which indicates that the particles capture much more light than is physically incident on them. Silver is also the only material whose plasmon resonance can be tuned to any wavelength in the visible spectrum.

From this statement the obvious advantages of silver, and the reason for its choice as a model nanoparticle for the novel synthesis of nanocomposite materials is clear. Silver nanoparticles have applications in many areas including biomedical, materials science, catalysis etc. Some of these are briefly discussed below:

1.4.2 Applications of Silver Nanoparticles

(a) Optical Sensors

Silver nanoparticles show a unique peak in absorption due to the SPR effect. This effect is caused by a collective excitation of the conduction band electrons of the nanoparticle during their interaction with the incident electromagnetic radiation which is already discussed in section 1.2.3. The value of maximum wavelength of this plasmon resonance peak depends upon the size and shape of nanoparticles as well as the host matrix. Due to this extraordinary optical characteristic, silver nanoparticles have large number of applications in photonics, sensors, colour filters etc. [43, 99-103].

(b) Catalyst

Another possible application of silver nanoparticles is their use as a catalyst. High surface area and high surface energy predetermine metal nanoparticles for being effective catalytic medium. Growing small particles of silver have been observed to be more effective catalysts than stable colloidal particles [104-105].
(c) **Antimicrobial Agent**

Since ancient times, silver is considered as a non-toxic, safe inorganic antibacterial agent capable of killing microorganisms that cause diseases. According to the mechanism reported, silver nanoparticles interact with the outer membrane of bacteria, and arrest the respiration and some other metabolic pathway that leads to the death of the bacteria. It has a significant potential for a wide range of biological applications such as antibacterial agents for antibiotic resistant bacteria, preventing infections, water filters to clean infected water and prevent diseases as well as wound dressings [106-107].

(d) **Surface Enhanced Raman Scattering**

Silver nanoparticles exhibit a phenomenon known as surface enhanced raman scattering (SERS) [108]. The SERS technique is a powerful analytical tool in the fields of surface science, biology, analytical chemistry, biochemistry, catalysis and materials research. The excellent sensitivity and selectivity of SERS allow for the determination of chemical information from single monolayer on planar surfaces and extend the possibilities of surface vibrational spectroscopy to solve a wide array of problems. The aggregation of silver nanoparticles is prerequisite for stronger SERS enhancement.

1.5 **Synthesis of Nanocomposites**

Material scientists are conducting research to develop novel materials with better properties, more functionality and lower cost than the existing ones. Several physical, chemical and biological synthesis methods have been developed to enhance the performance of nanocomposites displaying improved properties with the aim to have a better control over the particle size, distribution and morphology [109-111]. Synthesis of nanocomposites to have a better control over the particle size, distribution morphology, purity, quantity and quality by employing environment friendly economical processes has always been a challenge for the researchers [112]. Nanocomposites can be synthesized by various methods like low energy ion-beam mixing, sol-gel, direct metal-ion implantation, ion-exchange, vacuum deposition, field-assisted ion diffusion etc. [11-17, 62, 113-115]. Among the different methods for fabrication of silver-soda glass nanocomposites, vacuum deposition and ion-exchange are promising methods. Both these methods are easy to
handle, economical & consume less time, have minimal requirements for sample preparation, ease of adaptation to automated operation, have no residual solvents as in wet chemical synthesis processes.

1.5.1 **Vacuum Deposition Method**

Nowadays, vacuum deposition technique is routinely being used to form optical interference coatings, mirror coatings, decorative coatings, permeation barrier films on flexible packaging materials, electrically conducting films, wear resistant coatings and corrosion protective coatings [116]. This method can be effectively used for the synthesis of metal-glass nanocomposites. In this method a thin film of the metal intended to form nanostructures is grown on the host matrix by thermal evaporation.

**Advantages of Vacuum Deposition Method:**

1) Extreme versatility in composition of deposit. Almost any metal, alloy, refractory or intermetallic compound, some polymeric type materials and their mixtures can be easily deposited.

2) The ability to produce unusual microstructures and new crystallographic modifications.

3) Good adhesion can be achieved between thin film and substrate.

4) The substrate temperature can be varied within very wide limits.

5) The ability to produce coatings at high deposition rates with high purity.

6) This technique is relatively inexpensive compared to other physical vapour deposition techniques such as electroplating.

1.5.2 **Ion-Exchange Method**

Ion-exchange is a well-known technique proposed and developed since 1970s, to modify the electrical and optical properties of glass by embedding metal nanoparticles [14-15, 117-118, 119-152]. In this process, monovalent alkali ions on the surface layers of the glass are replaced by the ions of the same valence from the surrounding medium. Consequently, this replacement can change the refractive index of the host material.
Advantages of Ion-Exchange Method

1) Ion-exchange as a fabrication process promises simplicity, economy and optical fiber compatibility, not requiring complicated manufacturing equipment.

2) It allows for batch processing and also flexibility of process and glass choices, so it can be adapted for many applications such as optical limiters, optical sensing devices etc. [117-118].

Vacuum deposition and ion-exchange methods have been discussed in detail in chapter 2.

1.6 Modified Properties of Silver-Glass Nanocomposites and Related Literature

Intense research in the field of synthesis and study of composite materials containing metal nanoparticles is motivated by the rise of their various potential applications in diverse disciplines of science and technology [7-8, 43, 67-75]. Growth of nanoparticles under the surface of bulk material is a key technology in order to improve the quality and desired properties of the host glass matrix such as colour, refractive index, corrosion resistance, wear resistance, surface hardness etc. [3, 61-66]. Addition of metal nanoparticles in glass is responsible for the change in their structural, optical, electrical and mechanical properties. Based on these interesting aspects, synthesis of metal nanoparticles in glass has been studied by many research groups [5, 11-17, 113-115, 119-152]. In the literature, there are numerous reports paying more attention to the synthesis of silver metal nanoparticles in glass by ion-exchange and vacuum deposition methods followed by ion-irradiation, annealing in reduced atmosphere or in a high vacuum atmosphere [5, 11, 14-16, 76, 119-152]. A brief description of literature on synthesis methods is presented here.

Synthesis of silver nanoparticles in ion-exchanged soda glass followed by annealing in hydrogen reducing atmosphere have been studied by A. Miotello et al., C. Mohr et al., E. Borsella et al. and some other authors [119-125]. P. Gangopadhyay et al. and S. Bera et al. have reported synthesis of silver nanoparticles in glass matrix by ion-exchange and annealing in vacuum [126-128]. P. Magudapathy et al. and some other authors have made silver nanoparticles in glass by the combined use of ion-exchange and subsequent ion irradiation [15, 76, 129-135]. Formation of silver nanoparticles in ion-exchanged soda-lime glass in the
presence of Ar$^+$ laser beam has been studied by M. D. Niry et al. and A. Nahal et al. [14, 136]. H. Hofmeister et al. used ion, electron and laser irradiation of soda glass containing silver nanoparticles and discussed the obtained structure in terms of radiation effects [137]. Some authors reported growth of silver nanoparticles in ion-exchanged soda glass during laser irradiation [138-147].

P. Gangopadhyay et al. [11, 16] have discussed the growth of silver nanoparticles in soda glass matrix after irradiation with argon ions on silver thin films depositing by thermal evaporation. Xia Wu et al. [148] have studied optical properties of Ag-Bi$_2$O$_3$ nanocomposite films prepared by co-sputtering method followed by annealing at different temperatures. Formation of gold nanoparticles embedded in silica films using RF-magnetron sputtering technique with subsequent thermal treatment have been reported by A. Belahmar et al. [149]. Effect of air annealing on optical and structural properties of silver films prepared by thermal evaporation have been investigated by Jing Lv et al. [150-151]. A. Serrano et al. [152] have reported the formation of gold nanoparticles in soda glass by thermal evaporation method followed by annealing in air.

1.6.1 Optical Properties

Knowledge of optical characteristics (refractive index, dielectric constant, photoluminiscence etc.) of metal-glass nanocomposites is of immense importance due to their applications in fabrication of optical fibers, optical sensors, waveguides, integrated optics for communications etc. [42, 43, 67-75]. These applications of glasses can be further improved by modifying their properties [61-66]. Modifications of the glass properties can be achieved by modifying the bulk glass composition or by modifying the glass surface, affecting the whole performance of the glass product. Glass surface modification can be performed in different ways such as by adding materials to the original surface by vacuum deposition and ion-exchange techniques. Both techniques are relatively easy to perform and are used to alter the glass surface properties. Some previous studies have reported the tailoring of optical properties of glasses by vacuum deposition and ion-exchange techniques. Following section briefly describes some of the optical properties studied in the present endeavor.
(a) Colour

Optical properties of glass are characterized by the interaction of glass with electromagnetic radiation. Most types of glasses, partially absorb, reflect and transmit the incident light. The chemical composition of the glass matrix and its additives determine these properties. Most oxide glasses are coloured due to excitation of d-orbital electrons of transition metallic ions to a higher energy level. On the other hand, the mechanism of yellow colouration involves the scattering and absorption of incident light by the presence of “metallic” nanoparticles in the matrix [3, 34]. Mie theory explains that the presence of silver nanoparticles in the glass matrix can affect the transmission of light resulting in yellow colouration [29]. The introduction of silver nanoparticles into glass matrix strongly affects its optical properties. The change in optical properties can be attributed to the quantum confinement of electrons within nanoparticles and the surface plasmon resonance which has been discussed earlier in section 1.1.2.2 & 1.2.3 respectively.

Literature contains some reports on tuning of optical properties of silver-glass nanocomposites synthesized by the combined use of ion-exchange and subsequent thermal annealing in vacuum [126-127]. However, there are few reports available where annealing has been carried out in air but at very high temperatures and for long durations [153-154]. They have shown no shift in the surface plasmon resonance peak [126, 154-155]. Of practical relevance is the influence of annealing atmosphere on silver deposited glass substrate, a subject currently under discussion. In this regard, several authors have reported the vanishing of SPR peak of silver nanoparticles when composited are exposed to air and ascribed it to oxidation of nanoparticles [156-160]. They have also reported that annealing of silver doped films in air atmosphere at 450°C yielded colorless films containing silver oxide. These films turned yellow when heated in H₂–N₂ (reducing atmosphere) due to the formation of silver nanoparticles.

(b) Refractive Index

Refractive index is one of the most important optical constant of a material, which in general depends on the wavelength of the interacting electromagnetic wave, through a relationship called dispersion. Optical properties of nanocomposites are directly related to the refractive index ‘n’ which is a measure of the ability of the
glass to refract or bend light as it passes through the glass. In materials where an electromagnetic wave loses its energy during its propagation, the refractive index becomes complex. The complex refractive index, $n^*$, is defined by $n^* = n - ik$.

The real part is usually the refractive index ‘n’ and the imaginary part is called the extinction coefficient ‘k’. The optical constants $n$ and $k$ can be determined by measuring the reflectance from the surface of a material as a function of polarization and the angle of incidence. From normal incidence, the reflection coefficient, $r$, is obtained as [161]:

$$r = \frac{1 - n^*}{1 + n^*} = \frac{1 - n + ik}{1 + n - ik}$$  \hspace{1cm} (2)

The reflectance $R$ is then defined by:

$$R = |r|^2 = \left| \frac{1 - n + ik}{1 + n - ik} \right|^2 = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$  \hspace{1cm} (3)

To obtain refractive index equation (3) can be solved:

$$n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(R - 1)^2} - k^2}$$  \hspace{1cm} (4)

Extinction coefficient is related to the absorption coefficient ($\alpha$) and the wavelength ($\lambda$) by [161-163]:

$$K = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (5)

Further, refractive index is related to the relative dielectric constant $\varepsilon_r$ by using the standard result derived from Maxwell’s equations:

$$n^* = n - ik = \sqrt{\varepsilon_r} = \sqrt{\varepsilon_1 - i\varepsilon_2}$$  \hspace{1cm} (6)

where $\varepsilon_1$ and $\varepsilon_2$ are, respectively, the real and imaginary parts of $\varepsilon_r$. Equation (6) gives [162]:

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (7)

$$\varepsilon_2 = 2nk$$  \hspace{1cm} (8)
In relevance to optics, the real part of dielectric constant is closely related to the refractive index and the imaginary part is to the extinction coefficient which represents the losses of photon energy when optical wave propagates through the media. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optical devices such as switches, filters and modulators etc., where the refractive index of a material is the key parameter for device design.

The method of vacuum deposition and ion-exchange are effective tool for modifying the refractive index of glasses and can be successfully applied to form waveguide structures [164-165]. The ion-exchange technique has been utilized to modify optical constants like refractive index, dielectric constant of glass. J. R. Hensler et al. [166] have observed a method to increase the refractive index of alkali-silicate glass by diffusing ions of silver, copper, thallium etc. Changes in the refractive index of ion-exchanged glasses have also been observed by S. Ruschin et al., J. Albert et al., R. Oven and other authors [117, 167-171]. Previously some work has been done on silver-glass nanocomposites to study the increase in value of refractive index using ion-exchange technique but the changes observed in refractive indices were very small [117, 172].

Literature contains number of reports on photoluminescence of silver-glass nanocomposite glasses. E. Borsella et al. [125] have investigated spectral luminescence of silver in ion-exchanged soda-lime glass. They have also reported structural rearrangement of the Ag$^+$ ion environment with increasing silver nanoparticle concentration in glass [173]. Photoluminescence of silver nanoparticle glasses prepared by ion-exchange followed by annealing have been reported by O. Veron et al. [174]. Work on photoluminescence study of silver nanocomposite glasses is still in progress.

**1.6.2 Surface Hardness**

The most widely accepted definition for hardness is, “the ability of a material to resist permanent penetration. A hard material is generally defined as one which is not easily indented by a rigid body or as one which is difficult to scratch. The measurement of hardness of brittle materials is usually carried out with the help of Vickers or Knoop indentation at various loads. In general, an indenter is pressed
into the surface of the sample material to be tested under a specific load for a
definite time interval and a measurement is made of the size or depth of the
indentation. The force and size of the indentation can be related to a hardness which
can be objectively related to the resistance of the material to permanent penetration
[175].

Glass has a unique combination of desirable properties for various engineering
applications such as transparency, hardness, durability and low cost. However, its
use has always been limited due to its low tensile strength and resistance against
fracture, low hardness etc. For metal-glass composites, mechanical properties,
namely its hardness, can be improved significantly when the size of embedded metal
particles is reduced to less than a few nanometers. Microhardness is a complex
property, composed of mechanical characteristics and chemical bonding; it could
serve as a valuable guide in many engineering applications of the investigated
material. Glass with improved microhardness is used in military, motor, locomotive,
electronic and architectural sectors, information recording media application which
includes magnetic disks, optical magnetic disks and high density optical disks.
Different treatments can be applied to glass for modifying their mechanical
properties. Among different techniques, vacuum deposition and ion-exchange both
are simple and attractive techniques which provide the possibility to improve the
hardness of glass.

Literature contains only a small number of reports to investigate the surface
hardness of silver-glass nanocomposites. K. J. Berg et al. have measured the
changes in Vicker’s microhardness of silver exchanged glass [64]. M. Suszynska et
al. have studied the changes in Vicker’s microhardness of the ion-exchanged soda
glass [176]. They have also reported microhardness of copper doped soda lime silica
glass [177].

1.6.3 Electrical Conductivity Behaviour

The electrical properties of the nanocomposites are strongly influenced by the
metal filling factor and changes in the microstructure [178]. A critical filler loading
must be incorporated to transfer the composite from the insulating state into the
conducting state. At this critical concentration, which is known as the percolation
threshold, the electrical conductivity of the composite suddenly increases by several
orders of magnitude. Often at the percolation threshold, the filler forms a continuous network inside the host dielectric matrix and further increase in the filler loading usually has little effect on the composite electrical resistivity. However, if a remarkable decrease in the composite’s electrical resistivity is noticed with increasing the filler loading above the percolation threshold, this means that the three dimensional conductive network has not yet been formed at the percolation concentration, and thus the composites conductivity is due to tunneling in addition to direct contact between the particles. In some cases, tunneling could be the dominant mechanism. Tunneling conduction occur when the distance between the filler particles are close enough, roughly less than 10 nm. Investigating the current-voltage (I-V) relationship gives an indication whether the composite conductivity is due to tunneling or direct contact between the particles [179-180]. Very few reports are available in literature on electrical conductivity of silver-soda glass nanocomposites, nevertheless in one report P. Magudapathy et al. [129] have studied the variation in resistivity of silver nanoparticles embedded in glass with temperature.

1.7 Justification and Aim of the Present Work

It has been clearly revealed from the existing literature [7-8, 61-66] that the fabrication of nanocomposites of glass consisting of metal nanoparticles have recently received considerable interest as advanced technological material because of its drastically improved properties. As a result, their usage has increased tremendously for a variety of applications particularly in the fabrication of photonic devices, data storage systems, biosensors, waveguides, solar cells, aerospace, microelectronics etc. [43, 67-75].

Metal-glass nanocomposites can be synthesized by various techniques such as vacuum deposition, ion-exchange, low energy ion-beam mixing, sol-gel, direct metal-ion implantation, field-assisted ion diffusion etc. [11-17, 113-115]. Further, it is well established that vacuum deposition and ion-exchange techniques for synthesizing such nanocomposites are the most powerful and promising techniques as these are very less time consuming, economical and commercially viable. In the existing literature, reports are present on fabrication of metal-soda glass nanocomposites by using these techniques followed by long term heat treatment at high temperatures either in reducing atmosphere or in a high vacuum or by laser or
However, nanocomposites synthesized using these methods hardly show any shift in the surface plasmon resonance (SPR) band [126, 153-154, 181]. It is imperative to mention here that tuning of SPR band is essential for most of optical phenomenon like optical filters and surface enhanced fluorescence [182]. Besides this, many properties like optical absorption, reflection, transmission, refractive index, photoluminescence, dielectric, conduction mechanisms and surface hardness of such nanocomposites still remain unknown even despite numerous studies have been carried out in the past few years. Many researchers have studied some of the properties of metal-soda glass nanocomposites synthesized as above [119-152] by taking different metal nano filler for example silver, copper, gold etc. But most of these studies have been carried out in different contexts and in random manner. Moreover, synthesis of metal-soda glass nanocomposites by vacuum deposition method followed by thermal annealing in air and properties of thus formed nanocomposites have rarely been discussed.

Keeping above facts and prospects into consideration an effort has been made in the present research work to synthesize the silver-soda glass nanocomposites by using vacuum deposition and ion-exchange techniques both followed by thermal annealing in air and to investigate their structural, optical, mechanical and electrical properties. Here soda glass has been chosen as a host matrix due to its variety of applications in diverse fields, transparency and excellent matrix for growing small metallic particles. Silver metal as nano filler have been taken into consideration as they display surface plasmon resonance in the visible region besides their high conductivity and easy availability.

In the present 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 nanoparticles on structural, absorption, reflection, transmission, colour, refractive index, photoluminescence, dielectric, surface hardness and electrical conductivity behaviour of soda glass has been studied. The structural properties of prepared nanocomposites have been studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The optical properties of the synthesized nanocomposites have been characterized by UV-Visible spectroscopy and photoluminescence spectroscopy. Surface hardness measurements of silver-soda
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glass nanocomposite samples carried out using Knoop microhardness technique. The electrical conductivity behaviour of nanocomposites have been studied by two probe I-V measurement technique.

The area of glass-mediated assemblies of nanoparticles will definitely open up several new avenues for efficient and flexible nanofabrication with unique and varying combinations of properties and having high potential for successful commercial development.

1.8 Layout of Chapters

In addition to chapter 1 (introduction) the rest of the thesis is divided into following chapters:

Chapter 2: Materials and Experimental Techniques

This chapter gives a brief description of the experimental methods which we have used in the synthesis and characterization of silver-soda glass nanocomposites. In this chapter, we have given description of vacuum deposition and ion-exchange methods which have been used as synthesis methods in present research work. Also the description of the characterization techniques such as UV-Visible spectroscopy, Scanning electron microscopy, Transmission electron microscopy, Photoluminescence spectroscopy, I-V measurements, Microhardness measurements have been included to get information regarding optical, structural, electrical and mechanical properties.

Chapter 3: Results and Discussion

This chapter presents the results and discussion of the research work that has been carried out. It describes the preparation methods and studies related to the synthesis of silver-soda glass nanocomposites by vacuum deposition method and ion-exchange method followed by thermal annealing in air. These synthesized nanocomposites were characterized by various techniques such as UV-Visible spectroscopy, Scanning electron microscopy and Transmission electron microscopy to confirm the formation of silver nanoparticles in soda glass matrix. Different optical parameters like reflection, transmission, refractive index, real and imaginary parts of dielectric constant have been calculated and presented in details. The photoluminescence spectra, surface hardness and electrical conductivity behaviour
of these nanocomposites have also been discussed.

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

This chapter includes brief summary, major outcomes of the present investigations and conclusions along with suggestions for future scope of present work in this exciting area of research.
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