Chapter - 3

SIZE DEPENDENT OPTICAL ABSORPTION OF SINGLE AND BI-METALLIC NANOCLOUDS
3.1. INTRODUCTION

Modification of materials for enhancing their properties has become a growing part of the nanotechnology. Nanoparticles are introduced into a dielectric material (matrix) by various techniques, which in turn results in a nanoclusters that exhibit significant enhanced properties in comparison to its bulk. These nanoclusters not only exhibit enhanced electrical and thermal conductivities but also distinctive optical and dielectric properties due to their quantum size effects and surface effects [1-3].

The dimension of nanoclusters are only a few or tens of nanometers resulting in the confinement of the motion of electrons in three dimension space leading to discrete energy levels, that are different from that of their respective bulk metals. Hence laws of classical physics fail and quantum mechanics comes into play with better description of the properties of metal nanoclusters. The optical response of the nanoclusters depends on the nature of dopant and host matrix, geometry and concentration of the nanoclusters and the interacting wavelength of electromagnetic waves. The dependence of all these parameters makes it difficult to develop a general theory that can explain all features of the optical response.

This chapter emphasizes the size dependent optical absorption of the embedded metal nanoclusters in soda-lime glass. In specific the interaction of light with the embedded metal nanoclusters, along with the role of the size dependent dielectric function of the metal and host matrix on the optical absorption.
Maxwell-Garnett [4,5] was the first to make a theoretical approach to study the interaction of the light with metal aggregates by developing Lorentz’s [6] theory which discusses the optical properties of a medium containing small metallic spheres and found the results were in good agreement with the theoretically calculated optical absorption spectra. Debye [7] approached the same problem by calculating the mechanical pressure on small particles, which is due to the consequence of the interaction with light (light pressure), as a function of the dielectric constant and the electrical conductivity of the material.

Mie [8] started with a phenomenological approach without a physical description concerning the electron levels and electron motions inside the clusters. He divided the problem into two aspects. The first one is due to the electromagnetic problem starting from first principles and the second is materials problem due to the dielectric function, which can be obtained either by experimental results or theoretical evaluation. Mie’s theoretical approach to calculate the optical extinction involved the experimental results of Steubing [9], who studied optical absorption of gold particles of about 60 nm diameter in three different solutions. The results of Mie were convincing. The optical absorption spectra of the dielectric composites containing metal nanoclusters are characterized by the surface plasmon resonance (SPR) of the respective nano species, which is nothing but the collective plasmon oscillations of the valence electron cloud.

Kreibig [10,11] introduced the collective plasmon oscillations of different multiple order with an aim to interpret Mie theory. Such collective excitations are plasmon polaritons, excited by optical means, in contrast to free plasmons excited by fast electrons. Indeed as noted by Kreibig [12], the notation “plasmon” introduced for the Mie resonances was proposed by Schopper in analogy to the bounded gaseous plasmon oscillations.
3.2. SURFACE PLASMON RESONANCE OF SMALL CLUSTERS

An electromagnetic wave interacts with the conduction electrons that are confined to the small volume (~50 nm) of the metal particles embedded in the composite medium, the oscillating electric field causes these conduction electrons to perform collective motion with respect to the positively charged immobile ionic core, as shown in Fig. 3.1. Therefore the surface plasmon resonance (SPR) is the collective excitation of conduction electrons of the metal clusters when it is irradiated with a beam of light. The resonance peak occurs in the visible region for the noble metal clusters.

Surface plasmons are quanta associated with longitudinal waves propagating in matter through the collective motion of large numbers of electrons. Surface plasmons are a subset of these eigen modes of the electrons which are bound to regions in the material where the optical properties reverse, i.e., the interface between a dielectric and conducting medium. However, in the low ‘k’ vector limit, these surface modes couple with the free electromagnetic field to yield a polariton type excitation.

Fig. 3.1. Schematic representation of the surface plasmon oscillation of spherical metal nanoparticle
The principle consequence is that the quantum nature of the excitation is relaxed and it exists over the entire frequency range from zero to an asymptotic value determined by the classical surface plasmon energy. This means that surface plasmon polaritons can be accessed optically over a large frequency range and are typically evidenced by a resonant dip in the reflectance of the material under the correct coupling conditions. We currently use this resonant effect as a means of probing the optical properties of nanomaterials.

Optical absorption spectroscopy has been widely used on dielectric composites containing small metal particles because the location, width of the surface plasmon resonance (SPR) and amplitude give information of the nanocluster species, their size and size distribution. The theoretical background of the metal nanoclusters embedded in a dielectric medium is explained below.

3.3. THEORETICAL BACKGROUND OF SINGLE METAL NANoclUSTER

The dielectric function is one of the most informative and most commonly measured optical properties of the composite media. In certain circumstances, simplifying assumptions can be made so as to extract the dielectric properties of the particles of the composite. The simple analyses require that the particles must be small compared to the wavelength of the electromagnetic probe in the medium. The optical properties of materials are expressed using the dielectric function. If the extinction by scattering is small compared to the extinction by absorption, then the real and imaginary parts of $\varepsilon$ are given by $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2 nk$ where ‘n’ is the refractive index and ‘k’ the wave vector.
The absorption coefficient $\alpha$ is related to the imaginary part of the dielectric function by $\alpha = \frac{2\pi \varepsilon_2}{n\lambda}$ and $\lambda$ the wavelength of the incident light. Generally speaking the dielectric function of the metal nanoclusters can be calculated in a classical way by changing the relaxation time in the Drude free electron model and taking into account the confinement into clusters smaller than the mean free path of the electrons in the bulk material [13].

The optical absorption of the glass of dielectric constant $\varepsilon_m$ containing the metallic spheres of dielectric constant $\varepsilon$ and radius $R$ as shown schematically in Fig. 3.2 is usually expressed starting either from the Mie theory or from the Maxwell-Garnett effective medium theory [14].

![Fig. 3.2. Schematic representation of metal sphere embedded in glass matrix](image)

In the first case, the contribution of each cluster to the absorption is calculated, to obtain the absorption coefficient. In the second case, an effective dielectric function is calculated for the glass cluster colloid and the absorption coefficient is obtained from the imaginary part of this function.
Using the boundary conditions as the sphere surface, one can calculate the resulting polarization of the sphere as a whole due to the external field. The internal field is given as

$$E_i = E_0 \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}$$  \hspace{1cm} \ldots (3.1)$$

where $-\varepsilon_m$ is the dielectric constant of the embedding medium. The static polarizability of the sphere which is defined as $P = \varepsilon_m \alpha E_0$ is found to be

$$\alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$  \hspace{1cm} \ldots (3.2)$$

In the special case of metals we have $\varepsilon(0) = -\infty$ and this leads to the classical static electric polarizability $\alpha_{cl}$ of a metal sphere

$$\alpha_{cl} = 4\pi\varepsilon_0 R^3$$  \hspace{1cm} \ldots (3.3)$$

This solution of electrostatics applies as well to small metal spheres in oscillating electromagnetic fields in the quasi-static regime. This regime is characterized by keeping the time but not the spatial dependence of the electromagnetic field. In that, approximation excitations due to magnetic field do not occur. Replacing $\varepsilon$ and $\varepsilon_m$ of equations (3.1) and (3.2) with their frequency dependent values $\varepsilon(\omega)$ and $\varepsilon_m(\omega)$, we get the resonance behavior whenever

$$|\varepsilon + 2\varepsilon_m| = \text{Minimum}$$  \hspace{1cm} \ldots (3.4)$$

and $[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2 = \text{Minimum}$  \hspace{1cm} \ldots (3.5)$$
The resonance frequency can be established from the common relation \( \varepsilon_1 = -2\varepsilon_m \) using the free electron approximations and also \( \varepsilon_m = 1 \). The resonance position is given by

\[
\omega_1 = \frac{\omega_p}{\sqrt{3}} \quad \ldots \ (3.6)
\]

The above equation is sometimes also called as classical surface plasmon frequency. The term surface stems from the fact that although all electrons are oscillating with respect to the positive-ion background, the main effect producing the restoring force is the surface polarization.

### 3.4. MIE THEORY

Mie was the first to describe the optical absorption and elastic scattering by metallic spherical clusters \([8]\) within in the framework of electrodynamics. He applied Maxwell’s equations with appropriate boundary conditions in spherical coordinates using multiple expansions of the incoming electric and magnetic fields. Input parameters were the particle size and optical functions of the particle material and of the surrounding medium. His solution was based upon the determination of scalar electromagnetic potentials from which the various fields were derived. Solving the wave equation

\[
\Delta \pi + |k|^2 \pi = 0 \quad \ldots \ (3.7)
\]

in spherical coordinates:

\( \pi^\text{inc}_{\text{c.m}} \) is the incident plane wave,

\( \pi^\text{in}_{\text{c.m}} \) is the wave inside the cluster and

\( \pi^\text{sca}_{\text{c.m}} \) is the outgoing scattered wave
The indices e and m indicate the sets of electrical and magnetic partial waves, respectively. The solutions can be separated in spherical coordinate

\[ \pi = R(r)\Theta(\theta)\Phi(\phi) \]  \hspace{1cm} \cdots (3.8)

\[ \pi = \{\text{cylindrical fct.}\} \cdot \{\text{Legendre spherical fct.}\} \cdot \{\text{trigonometric fct.}\} \cdots (3.9) \]

The relevant parameter in all formulae is the size parameter \( x = |k|R \) which distinguishes the regime of geometrical optics \((x>>1)\) from clusters \((x<<1)\).

Mie’s extensive and lengthy derivations were essentially reduced by Born in his famous book on optics [15]. A different and more formal mathematical approach was introduced later by Stratton [16] and has now become more common than the original Mie version [17,18]. This fact needs to be emphasized since formally different expressions for the interaction cross sections result which might give rise to misunderstandings. In the latter description vector functions \( M, N \) and \( L \) are formally introduced which solve the wave equation and the divergency condition.

\[ L = \nabla \psi \]  \hspace{1cm} \cdots (3.10)

\[ M = \nabla \times (\Gamma \psi) \]  \hspace{1cm} \cdots (3.11)

\[ N = \frac{1}{|k|} \nabla \times M \]  \hspace{1cm} \cdots (3.12)

Here \(|k|\) denotes the wave vector and \( \Psi \) a scalar function. The \( E \) and \( H \) fields of both partial waves, which follow from \( M \) and / or \( N \) in analogy to the Mie potentials \( \Pi \). After the complete electrodynamic calculations, the simplified Mie formula predicting the absorption of metal clusters small compared to the wavelength of the incident light, embedded in a medium is
\[ \alpha = 9 \frac{\omega \varepsilon_m^{3/2}}{c} V \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2} \]  

… (3.13)

\[
V = \frac{4}{3} \pi R^3
\]

denotes the particle volume, \( \varepsilon_m \) is the dielectric function of the embedding medium and \( \varepsilon(\omega) \) the dielectric function of the particle material. The plasmon resonance occurs at the frequency where the denominator \([\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2\] takes its minimum. The condition is simplified to \( \varepsilon_1(\omega) = -2\varepsilon_m \) provided that \( \varepsilon_2(\omega) \) is small or does not vary much in the vicinity of the resonances.

The spectral features of equation (3.11) viz., position and shape of resonance, do not directly depend on the particle radius \( R \) but indirectly due to size dependencies of \( \varepsilon_{1,2}(\omega) \). Thus the resonance position height and width offer a suitable experimental tool to study the size dependencies of the dielectric functions also.

Hence Mie formalism allows the calculation of the absorption cross sections for particles small compared to the wavelength of incident probing light and account for a small fraction of the total volume [19].

3.5. OPTICAL MATERIAL FUNCTIONS OF NANOCLUSTERS

The dielectric functions of the metal nanoclusters can be calculated from the optical dielectric function of the bulk metals with necessary size corrections added to the Drude’s model.

3.5.1. Dielectric functions of metal nanoclusters

According to Drude’s theory, the plasmon resonance of bulk metals corresponds to the point where the free electrons can no longer shield the interior of the metal from the incident radiation. Thus the dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) of a system of \( N \) free electrons per unit volume can be written as
\[
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma \omega} = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i \frac{\omega_p^2}{\omega(\omega^2 + \Gamma^2)} \quad \ldots \ (3.14)
\]

where \( \omega_p = \left( \frac{4\pi N e^2}{m_e} \right)^{1/2} \) is the Drude plasma frequency. The relaxation constant \( \Gamma \) can be related to the electron mean free path \( L_f \) by \( \Gamma = \frac{V_F}{L_f} \) where \( V_F \) is the Fermi velocity of the electrons in bulk. For \( \omega \gg \Gamma \), the real and imaginary part of \( \epsilon(\omega) \) for free-electron metals can be written as

\[
\epsilon_1(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \quad \ldots \ (3.15)
\]

\[
\epsilon_2(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \Gamma \quad \ldots \ (3.16)
\]

Equations (3.15 and 3.16) illustrates that \( \omega \) equals the plasma frequency \( \omega_p \) for \( \epsilon_1(\omega) = 0 \). It is also called the volume plasmon frequency.

### 3.5.2. Mean free path effect

In the frame of classical electrical conductivity theory, the relaxation frequency of eqn. 3.14 for bulk material is composed of contributions \( \Gamma \) due to the interactions with phonons, electrons, impurities and lattice defects. This can be expressed by introducing the bulk mean free path \( L_f \) between memory canceling collisions of the electrons.

As long as these collisions are only slightly inelastic-dissipating only the excess energy or momentum due to an external field-solely electrons close to the Fermi surface contribute and hence
If the particle size becomes comparable or smaller than $L_f$, the included scattering processes may change. For example, the phonon spectrum depends on $R$ and special surface phonons may occur. As an additional scattering process, the collisions of the conduction electrons with the particle surfaces become important and in the frame of Matthiessen’s rule they are added to the former collision process [20,21].

The effective mean free path is then smaller than $L_f$ in all clusters with $2R \leq L_f$. This is called the free path effect. While theoretically predicted in 1939 [22] and 1954 [23], the free path effect was first observed in 1958 [24-26]. Hence the resulting dielectric function $\varepsilon(\omega, R)$ of the nanocluster can be obtained by replacing the relaxation function of (3.14) with (3.17).

\[
\varepsilon(\omega, R) = \varepsilon_{\text{bulk}}(\omega) + \omega_p^2 \left( \frac{1}{\omega^2 + \Gamma^2} - \frac{1}{\omega^2 + \Gamma(R)^2} \right) + i \frac{\omega_p^2}{\omega} \left( \frac{\Gamma}{\omega^2 + \Gamma(R)^2} - \frac{\Gamma}{\omega^2 + \Gamma^2} \right)
\]

… (3.18)

where $\Gamma(R) = \Gamma + \frac{V_F}{R}$ is size limited time and the term $\Gamma$ is the relaxation time in bulk material.

3.6. CLUSTER SIZE DETERMINATION

The average cluster radii $R$ of the embedded metal nanoclusters are calculated from the full width half maximum (FWHM, $\Delta \lambda$) of the SPR band of the optical absorption spectra. The inverse relation of the cluster radius $R$ to the FWHM, $\Delta \lambda$, is as given below:
\[ R = \frac{V_F \lambda_p^2}{2\pi C \Delta \lambda} \quad \ldots (3.19) \]

where \( V_F \) is the Fermi velocity of the electrons in the respective bulk metal, \( \Delta \lambda \) is the full width at half maximum of the absorption band and \( \lambda_p \) the characteristic wavelength at which surface plasmon resonance occurs. Both \( \lambda_p \) and \( \Delta \lambda \) depend on the substrate and size of the metal nanoclusters forming the composite.

The values of the mean free path, bulk plasma frequency and the Fermi velocity of some noble metals are shown in Table 3.1 with the measured values of FWHM from the absorption spectra and using the Fermi velocity of the metals the average size of the metal clusters can be calculated.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal</th>
<th>Mean free path ( L_f \times 10^{-6} \text{ m} )</th>
<th>Bulk Plasma frequency ( \omega_p \times 10^{15} \text{ Hz} )</th>
<th>Fermi velocity ( V_F \times 10^8 \text{ m/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ag</td>
<td>5.2</td>
<td>5.17</td>
<td>1.39</td>
</tr>
<tr>
<td>2.</td>
<td>Au</td>
<td>4.19</td>
<td>5.22</td>
<td>1.40</td>
</tr>
<tr>
<td>3.</td>
<td>Cu</td>
<td>3.84</td>
<td>7.48</td>
<td>1.57</td>
</tr>
</tbody>
</table>

**3.7. DETAILS OF THE UV-VIS-NIR SPECTROPHOTOMETER**

The optical properties of noble metal nanoparticles are different from the optical responses of their bulk or thin film forms. The theoretical optical absorption can be calculated by solving Maxwell’s equations for the scattering of electromagnetic waves of spherical objects, as carried out by Mie [27]. For the experimental results, the
absorption is usually obtained by directly recording the spectrum in an ultraviolet-visible (UV-VIS) range when the particles are excited with a UV-VIS light source. The spectrometer used to characterize surface plasmons in metal nanoclusters composite glasses (Shimadzu UV-VIS-NIR Model UV-3101 PC).

The UV-VIS (Shimadzu UV-VIS-NIR Model UV-3101 PC) spectroscopy probes the electronic transitions of a substance. When light or radiant power falls on a homogeneous medium, a part of the incident light is reflected, a part is absorbed and the remainder is transmitted. When the wavelength of the radiation through the sample is continuously varied, the absorbance versus wavelength plot gives absorption spectrum of the sample.

Figure 3.3 shows setup of UV spectrophotometer. It is a double beam, direct radiation measuring system. A halogen lamp is used as a near infrared source and a deuterium lamp for the UV-VIS source. A grating type double monochromator disperses the measuring light into its constituent wavelengths. The incident radiation is split into reference and sample beams by a chopper mirror.

Fig. 3.3. Schematic representation of setup of the UV spectrophotometer
The reference beam is used to nullify the effect of sample mount. The spectrophotometer employs two detectors depending upon the wavelength region a photomultiplier tube in the UV-VIS range and PbS cell in the near infrared region.

The wavelength resolution of the instrument is 0.1 nm. A thick aluminium plate with 1 mm diameter hole was used as sample holder. The absorbance was recorded for all the samples at room temperature in the wavelength range 200-1200 nm keeping the plain soda-lime glass as the reference. All the fibers and lenses used in the setup are carefully chosen to suit the wavelength range of the measurement. The spectra recorded were then analyzed using the peak fit software.

3.8. RESULTS AND DISCUSSION

Metal nanoclusters of few nanometers were formed into the soda-lime glass by binary ion exchanged method. The metal ion exchanged soda-lime glasses are furnace annealed at different temperature and laser annealed at various time duration. The theoretical optical absorption spectra were simulated using Mie’s formula (eqn. 3.13) for absorption of metal nanocluster. The absorption of metal nanocluster is small compared to wavelength of incident light, the absorption also depends on dielectric function of embedding medium and dielectric function of metal. The following topics are explaining the theoretical and experimental optical absorption spectra of copper, silver and gold nanocluster embedded in the soda-lime glass.

3.8.1. Copper nanoclusters

a) Copper nanocluster embedded in the soda-lime glass (Theoretical)

Theoretically simulated optical absorption spectra of copper clusters embedded in soda-lime glass of different radii using Mie theory is shown in Fig. 3.4.
For the purpose of convenience the spectra have been shifted vertically and the numbers indicated the radius of the clusters. These spectra clearly shows that the intensity of absorption spectra is vary with irrespective of cluster radius. Blue and red shift of SPR peak position is observed with increasing cluster radius. This change occurs in the absorption spectra are due the change in size dependent dielectric constant of (metal) copper cluster in the embedding medium.

b) Copper (Cu) nanocluster embedded in different medium (Theoretical)

The theoretically stimulated absorption spectra of copper nanoclusters embedded in different media (air, soda-lime glass, crown, sapphire) using Mie theory are shown in Fig. 3.5. The optical constants of medium and that of the different metals were taken from the literature [28].
Fig. 3.5. Theoretically simulated (Mie) optical absorption spectra of copper nanoclusters embedded in different media

From the theoretical simulated absorption spectra the SPR peak position of copper nanocluster varying depends on the embedding medium. It clearly shows that, the dielectric constants of the copper cluster (size dependent dielectric constant) are different for different embedding medium. The change in dielectric constant of embedding medium also changes the SPR peak value copper cluster.

c) Copper nanocluster (Theoretical and experimental)

The theoretically calculated absorption spectra with the experimentally recorded one are shown in Fig. 3.6. The figure showed a good match between theory and experiment, confirming the presence of copper clusters in glass matrix.
Fig. 3.6. Experimentally recorded and theoretically calculated absorption spectra of copper nanocluster embedded in soda-lime glass

d) Copper nanocluster embedded in soda-lime glass - furnace annealed

Copper nanoclusters of a few nanometers were formed into the soda-lime glass by ion exchange technique. The ion exchanged samples turned pale reddish brown due to presence of copper ions (Cu$^+$). Figure 3.7 shows the typical optical absorption spectra of copper ion (Cu$^+$) exchanged and different temperature annealed samples.

From the optical absorption spectra, it is found that absorption band edge ranges from 562 to 570 nm, and these absorption peaks correspond to the surface plasmon resonance (SPR) of copper clusters [29,30]. The spectra follow the trend of decreasing intensity with increasing wavelength. The average copper clusters sizes calculated using the equation (3.19) for various annealing temperatures are show in Table 3.2 shows that, copper cluster sizes vary from 4.41 nm to a maximum of 5.50 nm. But with increasing in annealing temperatures the size of cluster vary randomly without any trend.
Fig. 3.7. Experimentally recorded optical absorption spectra for plain, copper ion exchanged and different temperature annealed soda-lime glasses.

Table 3.2. Calculated cluster size (R), FWHM (Δλ) and SPR peak (λ_p) of furnace annealed copper ion exchanged and different temperature annealed soda-lime glasses.

<table>
<thead>
<tr>
<th>Annealing Temperatures (°C)</th>
<th>Cluster radius of Cu (R) (nm)</th>
<th>FWHM (Δλ) (nm)</th>
<th>SPR peak (λ_p) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-Annealed</td>
<td>5.29</td>
<td>50.56</td>
<td>567.18</td>
</tr>
<tr>
<td>100</td>
<td>5.00</td>
<td>53.474</td>
<td>566.63</td>
</tr>
<tr>
<td>200</td>
<td>5.50</td>
<td>48.012</td>
<td>562.51</td>
</tr>
<tr>
<td>300</td>
<td>4.41</td>
<td>59.91</td>
<td>562.98</td>
</tr>
<tr>
<td>400</td>
<td>5.315</td>
<td>50.66</td>
<td>568.48</td>
</tr>
</tbody>
</table>

Figure 3.8 represents the variation of cluster size with annealing temperature. The clusters size increases and decreases at various annealing temperatures. This indicates that during the annealing process, aggregation and segregation of Cu ions into the Cu ion exchanged soda-lime glasses.
Fig. 3.8. Plot of cluster radius versus annealing temperatures of copper ion exchanged and different temperature annealed soda-lime glasses

Figure 3.9 represents the plot of SPR peak position and FWHM versus the annealing temperature. A blue shift of SPR peak position is observed with increasing annealing temperatures. But in the case of 300 and 400°C annealed temperature, the red shift of SPR peak is observed.

Fig. 3.9. Plot of FWHM and SPR peak position versus annealing temperatures of copper ion exchanged and different temperature annealed soda-lime glasses
These shifting of SPR peaks are due to the change in clusters size during the annealing process, where a decrease of FWHM with increase in the SPR peak value is observed. This is also clearly shown in Fig. 3.9.

A plot of the SPR peak position and FWHM Vs. the cluster size is shown in Fig. 3.10. The red shift of SPR peak is observed with increasing cluster size. Irrespectively, blue-shift SPR peak is also observed for increasing cluster size this is due to lower value (48.02 nm) of FWHM. The FWHM value decreases significantly with increases in cluster size. The size dependency of the width of the plasmon resonance is well depicted in the plot of FWHM versus cluster radius. The FWHM decreases significantly with increases in cluster size. This kind of decrease in FWHM with increase in cluster size is due to the mean free path effect which comes into play for smaller (R ≤ 10 nm) cluster.

![Fig. 3.10. Plot of FWHM and SPR peak position versus cluster radius of copper ion exchanged and different temperature annealed soda-lime glasses](image-url)
e) Copper nanocluster embedded in soda-lime glass - laser annealed

Copper ion exchanged soda-lime glass samples were Laser irradiated by different exposure timings from 500 to 2000 ms in steps of 500 ms. Figure 3.11 shows the typical optical absorption spectra of copper ion exchanged and laser annealed samples. From the optical absorption spectra, it is found that absorption band edge ranges from 562 to 570 nm, and these absorption peaks correspond to the surface plasmon resonance (SPR) of copper clusters [29,30].

![Absorption Spectra](image)

**Fig. 3.11.** Experimentally recorded optical absorption spectra for copper ion exchanged soda-lime glasses with different laser exposure timings

**Table 3.3.** Calculated cluster size (R), FWHM (Δλ) and SPR peak (λ_p) value of copper ion exchanged soda-lime glasses with different laser exposure timings

<table>
<thead>
<tr>
<th>Laser exposure timings (ms)</th>
<th>Cluster radius of Cu (R) (nm)</th>
<th>FWHM (Δλ) (nm)</th>
<th>SPR peak (λ_p) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>6.30</td>
<td>41.92</td>
<td>561.58</td>
</tr>
<tr>
<td>1000</td>
<td>4.50</td>
<td>56.26</td>
<td>562.16</td>
</tr>
<tr>
<td>1500</td>
<td>5.80</td>
<td>46.69</td>
<td>570.33</td>
</tr>
<tr>
<td>2000</td>
<td>5.42</td>
<td>48.58</td>
<td>562.50</td>
</tr>
</tbody>
</table>
The average copper clusters sizes calculated using the equation (3.19) for various laser annealing time are shows in Table 3.3. Seen from the table (Table 3.3), the copper cluster sizes vary from 4.50 nm to a maximum of 6.30 nm. But with increasing the laser annealing time durations the size of cluster vary randomly without any trend. Figure 3.12 represents the variation of cluster size with the laser annealing time.

![Plot of cluster radius versus different laser exposure timings of copper ion exchanged soda-lime glasses](image)

**Fig. 3.12.** Plot of cluster radius *versus* different laser exposure timings of copper ion exchanged soda-lime glasses

When the laser annealing time gradually increases, the cluster sizes either increase or decrease this indicates that during the laser annealing process, aggregation and segregation of Cu ions into the Cu ion exchanged glasses.

Figure 3.13 represents the plot of SPR peak position and FWHM *versus* the different laser annealing time. A red and blue shift of SPR peak position is observed by increasing laser annealing time. These shifting of SPR peaks occur due to the change in clusters size during the laser annealing process, where the decrease of FWHM with increase in the SPR peak value is observed. This is also clearly shown in the Fig. 3.12.
**Fig. 3.13.** Plot of FWHM and SPR peak value versus different laser exposure timings of copper ion exchanged soda-lime glasses

A plot of the SPR peak position and FWHM Vs. the cluster size is shown in Fig. 3.14. The red and blue shift of SPR peak is observed with increasing cluster size. Irrespectively, blue-shift SPR peak is also observed for increasing cluster size this is due to lower value of FWHM. The FWHM value decreases significantly with increases in cluster size.

The size dependency of the width of the plasmon resonance is well depicted in the plot of FWHM versus cluster radius. The FWHM decreases significantly with increases in cluster size. This kind of decrease in FWHM with increase in cluster size is due to the mean free path effect which comes into play for smaller (R $\leq$ 10 nm) cluster. Both the furnace annealed and laser annealed copper (Cu) nanocluster shows the same trend of absorption spectra. The size variation in the furnace annealed Cu nanocluster is very less compared to laser annealed Cu nanocluster and also the 500 ms laser annealed Cu nanocluster having the large cluster size (6.30 nm).
3.8.2. Silver nanoclusters

a) Silver (Ag) nanocluster embedded in single medium (Theoretical)

Theoretically simulated optical absorption spectra of embedded silver clusters of different radii, using Mie theory are shown in Fig. 3.15. To highlight the difference, the spectra have been shifted vertically and the numbers indicated are the radius of the clusters. These spectra clearly show that there is no significant change in SPR peak position of silver nanocluster of different radius.
The theoretically simulated optical absorption spectra of embedded silver nanoclusters of different medium, using Mie theory is shown in Fig. 3.16. The spectra show that the SPR peak value depends on embedding medium. The optical absorption of metal silver nanocluster depends on dielectric constant silver and the dielectric constant of embedding medium.

The SPR peak positions of silver nanocluster are different for different embedding medium. It clearly shows that the SPR peak position silver nanocluster not only depends on dielectric constant of metal and also the dielectric constant of embedding medium. Blue and red shift of SPR peak position is observed with increasing the dielectric constant of embedding medium.
c) Silver nanocluster (Theoretical and experimental)

As a comparison, the theoretically (Mie) simulated and experimentally recorded optical absorption spectra of silver ion exchanged and annealed glass is shown in Fig. 3.17. The figure shows a good match between theory and experiment, confirming the presence of silver clusters in glass matrix.

From the experiment and theoretically recorded absorption spectra we confirming that the SPR band at 425 nm is due to the silver nanoclusters embedded in glass matrix as reported earlier [31-34].
d) Silver nanocluster embedded in soda-lime glass - furnace annealing

The optical absorption spectrum of the plain soda-lime glass, silver ion exchanged and different temperature annealed glasses is shown in Fig. 3.18. The optical absorption is due to collective oscillation of the conduction electron with respect to the ionic background in nanoscale silver cluster [35,36]. The Ag ion exchanged sample before annealing does not show any absorption peaks but after annealing the Ag ion exchanged samples shows a characteristic surface plasmon resonance (SPR) of Ag nanoclusters around 430 nm.

This result indicates that the diffused silver (Ag) ions stay scattered inside the dielectric matrix as silver (Ag) particles and the cluster growth is induced by coagulation during annealing. Increasing the annealing temperature leads to much higher absorption as well as a red shift of this band. In the case of 300°C annealed ion exchanged sample shows low absorption as well as moves to blue shift of the band, due to low cluster radius. The average silver clusters sizes calculated using the equation (3.19) for various annealing temperatures are show in Table 3.4.
Fig. 3.18. Experimentally recorded optical absorption spectra for plain, silver ion exchanged and different temperature annealed soda-lime glasses

Table 3.4. Calculated cluster size (R), FWHM (Δλ), SPR peak (λ_p) of different temperature annealed silver nanoclusters in soda-lime glass

<table>
<thead>
<tr>
<th>Annealing Temperatures (°C)</th>
<th>Cluster radius Ag (R) (nm)</th>
<th>FWHM Δλ (nm)</th>
<th>SPR peak λ_p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.96</td>
<td>138.73</td>
<td>424.32</td>
</tr>
<tr>
<td>200</td>
<td>1.20</td>
<td>116.74</td>
<td>429.29</td>
</tr>
<tr>
<td>300</td>
<td>0.82</td>
<td>158.33</td>
<td>420.53</td>
</tr>
<tr>
<td>400</td>
<td>1.16</td>
<td>117.25</td>
<td>429.32</td>
</tr>
</tbody>
</table>
Figure 3.19 represents the variation of cluster radius with annealing temperature. When the annealing temperature increases the cluster radius also increase but in the case of 300°C annealed samples the size of clusters radius decreases. This indicates that during the annealing process aggregation and segregation of silver ions in the ion exchanged glasses are observed.

![Graph of cluster radius versus annealing temperature.](image)

**Fig. 3.19. Plot of cluster radius versus annealing temperatures of silver ion exchanged and different temperature annealed soda-lime glasses**

Figure 3.20 shows the plot of SPR peak position and FWHM versus annealing temperature. In silver ion as exchanged soda-lime glass, the diffused silver (Ag) ions stay scattered inside the dielectric matrix as silver (Ag) particles and the cluster growth is induced after annealing. The plot explains variation of cluster size only after annealing. Blue and red shift of SPR peak position is observed with increasing annealing temperature. The blue shift of SPR peak position is observed at 100°C and 300°C annealed temperatures. The red shift of SPR peak position observed at 200°C and 400°C annealed temperature.
These shifting of SPR peaks were due to the change in cluster size during the annealing processes. Where a decrease of FWHM with increase in the SPR peak value, this is also clearly shown in Fig. 3.20.

![Plot of FWHM and SPR peak value versus annealing temperatures of silver ion exchanged and different temperature annealed soda-lime glasses](image)

**Fig. 3.20.** Plot of FWHM and SPR peak value *versus* annealing temperatures of silver ion exchanged and different temperature annealed soda-lime glasses

A plot of SPR peak position and FWHM versus the cluster size is shown in Fig. 3.21. Blue shift of SPR peak is observed with increasing cluster size. The size dependency of the width of the surface plasmon resonance is well depicted in the plot of FWHM versus cluster radius Fig. 3.21.

The FWHM value decreases significantly with increases in cluster size. This kind of decrease in FWHM with increase in cluster size is due to the mean free path effect which comes into play for smaller (R ≤10 nm) cluster as observed from copper clusters.
e) Silver nanocluster - laser annealing

Similar to copper, silver ion exchanged glasses were laser annealed for different exposure time and their respective optical absorption spectra are shown in Fig. 3.22. The silver (Ag) ion exchanged laser annealed samples shows a characteristic surface plasmon resonance (SPR) of Ag nanoparticles around 430 nm.

The laser annealed Ag ion exchanged samples shows a characteristic surface plasmon resonance (SPR) of Ag nanoparticles around 427 nm. This result indicates that the 500 and 1500 ms laser annealed sample having sharp peak due to growth of the silver clusters, but the 1000 and 2000 ms laser annealed sample shows broad peak due to desperation of the clusters. Increasing the laser annealing time leads to lower absorption as well as red and blue shift of this band.
Fig. 3.22. Experimentally recorded optical absorption spectra for silver ion exchanged soda-lime glasses with different laser exposure timings

The average silver clusters sizes calculated using the equation (3.19) for various laser annealing time are show in Table. 3.5

Table 3.5. Calculated cluster size (R), FWHM ($\Delta\lambda$) and SPR peak ($\lambda_p$) of laser annealed silver ion exchanged soda-lime glasses with different laser exposure timings

<table>
<thead>
<tr>
<th>Laser exposure time (ms)</th>
<th>Cluster Radius Ag (R) (nm)</th>
<th>FWHM ($\Delta\lambda$) (nm)</th>
<th>SPR peak ($\lambda_p$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.829</td>
<td>154.13</td>
<td>416.25</td>
</tr>
<tr>
<td>1000</td>
<td>0.426</td>
<td>257.61</td>
<td>385.89</td>
</tr>
<tr>
<td>1500</td>
<td>0.729</td>
<td>185.07</td>
<td>427.71</td>
</tr>
<tr>
<td>2000</td>
<td>0.394</td>
<td>273.62</td>
<td>382.29</td>
</tr>
</tbody>
</table>
Figure 3.23 represents the variation of cluster radius with different laser annealing time. When the laser annealing time duration increases the cluster radius also increase and as well decreases. This result indicates that during the laser annealing process aggregation and segregation of silver ions in the silver ion exchanged glasses are observed.

![Cluster Radius vs Laser Exposure Time](image)

**Fig. 3.23. Plot of cluster radius versus different laser exposure timings of silver ion exchanged soda-lime glasses**

Figure 3.24 shows the plot of SPR peak position and FWHM versus laser annealing time. The blue and red shift of SPR peak position is observed with increasing laser annealing time. The blue-shift of SPR peak position is observed at 1000 and 2000 ms laser annealing time. The red shift of SPR peak position observed at 500 and 1500 ms annealing time. These shifting of SPR peaks were due to the change in cluster size during the annealing processes. Where a decrease of FWHM with increase in the SPR peak value, this is also clearly shown in Fig. 3.24.
Fig. 3.24. Plot of FWHM and SPR peak value versus different laser exposure timings of silver ion exchanged soda-lime glasses

A plot of SPR peak position and FWHM versus the cluster size of Ag laser annealed sample is shown in Fig. 3.25. Blue and red shift of SPR peak is observed with increasing cluster size. The size dependency of the width of the surface plasmon resonance is well depicted in the plot SPR peak position and FWHM versus cluster radius Fig. 3.25.

The FWHM value decreases significantly with increases in cluster size. This kind of decrease in FWHM with increase in cluster size is again due to the mean free path effect which comes into play for smaller (R \leq 10 \text{ nm}) cluster as observed for earlier systems.
Fig. 3.25. Plot of FWHM and SPR peak value versus cluster radius of silver ion exchanged soda-lime glasses with different laser exposure timings

Both the furnace annealed and laser annealed silver (Ag) nanocluster shows the same trend of absorption spectra. The sizes of clusters are greater for the furnace annealed Ag nanocluster embedded in the soda-lime glass, compared to laser annealed Ag nanocluster.

3.8.3. Gold nanoclusters

a) Gold nanocluster embedded in soda-lime glass

A good amount of work had already been done on formation of gold in different matrices by direct implantation [37-42]. But we simulate absorption spectra gold (Au) nanocluster embedded in soda-lime glass using Mie theory.
Theoretically calculated optical absorption spectra of embedded gold clusters of different radii using the Mie theory is shown in Fig. 3.26. For the purpose of convenience the spectra have been shifted vertically and the numbers indicated the radius of the clusters. It can be shown that the SPR band is corresponding to gold nanocluster.

![Absorption Spectra](image.png)

Fig. 3.26. Theoretically simulated (Mie) optical absorption spectra of gold nanoclusters embedded in soda-lime glass

b) Gold (Au) nanocluster embedded in different medium (Theoretical)

The theoretically stimulated absorption spectra of gold nanoclusters embedded in different media (air, soda-lime glass, crown, sapphire) using Mie theory are shown in Fig. 3.27.
Optical constants of the various media and that of the gold metal were taken from the literature [28]. From the theoretical simulated absorption spectra the SPR peak position of gold nanocluster depends on the embedding medium. It clearly shows that, the dielectric constants of the gold cluster (size dependent dielectric constant) are different for different embedding medium. The change in dielectric constant of embedding medium also changes the SPR peak value gold cluster. Red and blue shift of SPR peak position is observed with increasing the dielectric constant of embedding medium. These shifting of SPR peaks were due to not only the change in dielectric constant of metal and also the nature of the media.
3.9. BI-METALLIC NANOCLUSTERS

Synthesis of bimetallic nanoclusters (core shell or alloy) can be done by different methods, such as the electrochemical method, radiolysis of aqueous solutions, hydrogen arc plasma and laser vaporization co-deposition. Bimetallic nanoclusters are produced by binary ion exchange method. In this the bimetallic nanocluster are produced by either sequential ion exchange or sequential ion exchange followed by suitable thermal treatments like furnace annealing or laser irradiation to varying the sizes of bimetallic (size of core and shall) nanocluster.

Thus in the present study, Cu-Ag, and Ag-Cu nanoclusters were formed in the same soda-lime glass matrix and their optical absorption are discussed in detail. As an introduction to it, a comparative plot of SPR bands of embedded copper, and silver nanoclusters were shown in Fig. 3.28.

![Absorption vs Wavelength](image)

**Fig. 3.28.** Comparative plot of absorption versus wavelength for copper and silver nanoclusters embedded in soda-lime glass
3.10. CORE-SHELL STRUCTURE OF BI-METALLIC NANOCLUSTERS

The core-shell materials can be semiconductors, metal or dielectrics. Zhikun Zhang et al. [43] had studied the thin shell structure of iron nanoparticles. The effective dielectric responses of nonlinear coated composites were discussed by Chen Xu and Zhen-ya Li [44]. Bilayered platinum coated gold and gold coated platinum clusters were formed in aqueous solution by Remi et al. [45]. Core-shell nanostructures were also formed by sequential ion implantation of two different metals [46]. Strobel et al. [47] made some predictions using kinetic lattice Monte Carlo simulations whether core-shell structures can be formed by sequential ion implantation.

Formation of bimetallic Cu-Ag and Ag-Cu nanoclusters is achieved by the sequential ion exchange technique followed by furnace annealing and laser irradiation for different exposure timings. Pre cleaned soda-lime glass is first dipped in the molten copper salt bath first and then again dipped in the molten salt bath of silver for Cu-Ag ion exchange. The process is repeated in the reverse manner with the dipping being done in the silver bath first and then in the copper bath for the Ag-Cu ion exchange.

The Cu-Ag and Ag-Cu ion exchanged samples were then cleaned and then furnace annealed or irradiated with laser for different exposure time. Optical absorption spectra of the laser annealed samples were recorded in the wavelength range of 200-1200 nm at room temperature.

3.11. THEORETICAL BACKGROUND OF BI-METALLIC NANOCLUSTERS

For the core shell structure of spherical nanoclusters, we first start with considering the case of an ellipsoid and then implying necessary conditions to the final equation, the polarizability of the coated sphere is obtained. Let us first consider the permittivity of an the inner core ellipsoid as $\varepsilon_1$, with semiaxes $a_1$, $b_1$, $c_1$; the permittivity of the outer shell as $\varepsilon_2$, with semiaxes $a_2$, $b_2$, $c_2$ embedded in a medium of permittivity $\varepsilon_m$. 
The schematic diagram of the core-shell spherical nanostructure embedded in a medium is depicted in Fig. 3.29.

![Schematic diagram of the core-shell spherical nanostructure](image)

**Fig. 3.29. Schematic representation of the a core-shell nanoparticle embedded in a dielectric medium**

In the case of core-shell particles contain additional internal boundaries for which electrodynamic boundary conditions have to be fulfilled separately. Special plasmon polaritons modes can therefore be excited in the core as well as in the shells and they couple strongly via their interfaces, resulting in complex extinction spectra [48-51].

Introducing the ellipsoidal coordinates \( \xi, \eta, \zeta \).

\[
\frac{x^2}{a_1^2 + \xi} + \frac{y^2}{b_1^2 + \xi} + \frac{z^2}{c_1^2 + \xi} = 1
\]

… (3.20)

where \( -c_1^2 \xi(\infty) \), with similar expressions for \( \eta \) and \( \zeta \). Therefore, \( \xi = 0 \) is the equation of the surface of the inner ellipsoid and \( \xi = 1 \) is that of the surface of the outer ellipsoid, where \( a_1^2 + t = a_2^2, \ b_1^2 + t = b_2^2, \ c_1^2 + t = c_2^2 \).

The potential of the applied field, which we take to be parallel to the z axis, is

\[
\Phi_\circ = -E_\circ z = -E_\circ F_\xi(\xi)G(\eta, \zeta)
\]

… (3.21)
The potentials $\Phi_1$ and $\Phi_2$ in the inner and outer ellipsoids, respectively are

\[\Phi_1 = C_1 F_1(\xi) G(\eta, \zeta), \quad -c_1^2 < \xi < 0 \quad \ldots \quad (3.23)\]

\[\Phi_2 = [C_2 F_1(\xi) + C_3 F_2(\xi)] G(\eta, \zeta), \quad 0 < \xi < t \quad \ldots \quad (3.24)\]

\[F_2(\xi) = F_1(\xi) \int_{c_1^2}^{\infty} \frac{dq}{(c_1^2 + q) f_1(q)}, \quad \ldots \quad (3.25)\]

\[f_1(q) = [(a_1^2 + q)(b_1^2 + q)(c_1^2 + q)]^{1/2}. \quad \ldots \quad (3.26)\]

The potential $\Phi_3$ in the surrounding medium is the sum of $\Phi_0$ and the perturbing potential $\Phi_p$ of the particle:

\[\Phi_p = C_4 F_2(\xi) G(\eta, \zeta) \quad \ldots \quad (3.27)\]

The requirement that $\Phi$ and $\frac{\partial \Phi}{\partial \xi}$ be continuous at boundaries gives us four linear equation in the unknown constants $C_1, C_2, C_3, C_4$, the solution to which yields the polarizability

\[\alpha_3 = \frac{\nu ((\epsilon_3 - \epsilon_m) \epsilon_2 + (\epsilon_1 - \epsilon_2)(L_3^{(1)} - f L_3^{(2)})) + f \epsilon_2 (\epsilon_1 - \epsilon_2))}{[\epsilon_2 + (\epsilon_1 - \epsilon_2)(L_3^{(1)} - f L_3^{(2)})\epsilon_m + (\epsilon_2 - \epsilon_m)L_3^{(2)}]} \quad \ldots \quad (3.28)\]

where $\nu = \frac{4 \pi a_1 b_1 c_2}{3}$ is the volume of the particle, $f = \frac{a_1 b_1 c_1}{a_2 b_2 c_2}$ is the fraction of the total particle volume occupied by the inner ellipsoid, $L_3^{(1)}$ and $L_3^{(2)}$ are the geometrical factors for the inner and outer ellipsoids:
\[ L^{(k)} = \frac{a_k b_l c_k}{2} \int_{b}^{\infty} \frac{dq}{(e^2 - q) f_k(q)} \quad (k=1,2). \]  

As a special case in the case of coated sphere \( (L^{(i)} = L^{(j)} = \frac{1}{3}) \), for which \( c_1 = c_2 = c_3 = \alpha \) and thus the polarizability of a coated sphere is given by the equation below

\[
\alpha = 4\pi a_2^3 \left( \frac{\varepsilon_2 - \varepsilon_m (\varepsilon_1 + 2\varepsilon_2) + f(\varepsilon_1 - \varepsilon_2) (\varepsilon_m + 2\varepsilon_2)}{(\varepsilon_2 + 2\varepsilon_m)(\varepsilon_1 + 2\varepsilon_2) + f(2\varepsilon_2 - \varepsilon_m)(\varepsilon_1 - \varepsilon_2)} \right) \quad \ldots (3.30)
\]

From the above equation the polarizability and hence the absorption spectra of the core-shell nanostructures can be calculated using the dielectric constants of the respective core, shell and the embedding medium. In the continuing part we reveal some interesting experimental optical absorption spectra of some core shell nanostructures synthesized by sequential ion exchange followed by suitable treatments or by combined ion exchange techniques. The experimental results were compared with the theoretically calculated spectra.

### 3.12. COPPER COATED SILVER NANOCLUSTER (Ag CORE Cu SHELL)

Copper coated silver (Cu-Ag) nanocluster is prepared by the copper ion exchange glasses are again dipped in the silver bath for the silver ion exchange for the same time of dipping. The ion exchanged glasses were then subjected to different treatments like furnace annealing and laser annealing.

The absorption spectra resembled the one Cu coated Ag nanocrystals in silica formed by sequential implantation of Ag\(^+\) and Cu\(^+\) ions with, TEM analysis depicting the diffracting rings of the core and shell materials [46]. The Fig. 3.30 shows the
sequential Cu-Ag ion exchanged sample with the spectra exhibiting SPR peak due the copper clusters alone. Post annealing of the copper coated silver (Cu-Ag) ion exchanged samples resulted in the evolution of another peak centered at 420 nm with a shoulder at 565 nm (Fig. 3.31).

Fig. 3.30. Optical absorption versus wavelength of sequential Cu-Ag ion exchanged soda-lime glass

Theoretical spectra were calculated using the equation (3.30) and were compared with the experimentally recorded one as shown in Fig. 3.31. The spectra showed a match between theory and experiment.
Fig. 3.31. Experimentally recorded and theoretically calculated optical absorption spectra of sequential (Ag-Cu core shell) ion exchanged soda-lime glass

a) Copper coated silver nanocluster embedded in soda-lime glass (constant Ag core different Cu shell thickness)

The dependency of the absorption spectra on the thickness of the coated material, the theoretical spectra is simulated using Mie theory by keeping the core size is constant and varying the shell (thickness) size or embedded copper coated silver nanoclusters and is shown in Fig. 3.32.

The numbers in bracket show the size of the core and shell clusters. The simulated spectra have sharp peak for Ag cluster and small hump for Cu cluster for copper coated silver nanocluster (Cu-Ag). Thus the size dependency of the absorption spectra of the core-shell structures is very well observed from the above spectra.
b) Copper coated silver nanocluster embedded in soda-lime glass (Ag core Cu shell) - furnace annealed

The experimentally recorded optical absorption spectra for Ag core Cu shell of (Cu-Ag) different temperature annealed samples as shown in Fig. 3.33. From the absorption spectra the shape of the spectra vary with different annealing temperature which is the result the SPR band due to the copper shell is very weakly seen for the lower annealing temperatures, but for the 650°C annealed sample a well resolved significant peak is observed for both the core and shell structures. The inset of the figure clearly shows the significant both silver core and copper shell of 650°C annealed (Cu Ag) ion exchanged sample.
Fig. 3.33. Experimentally recorded optical absorption spectra of Cu-Ag (Ag core/Cu shell) sequential ion exchanged and different temperature annealed soda-lime glasses.

c) Copper coated silver (Cu-Ag) - laser annealed nanocluster (Ag core Cu shell)

The experimentally recorded optical absorption spectra for Ag core of Cu shell of various laser annealed time samples as shown in Fig. 3.34. The spectra shows that there are two surface plasmon resonance (SPR) peaks one centered at 420 nm due to silver and another shoulder centered at 564 nm due to the copper clusters. For various laser exposure timings the spectra has slight shift in their peak positions which may be due to the variation in the concentration of the respective metal species. Since the SPR peak position depends on the concentration of the respective metal species.

Hence it can be very well confirmed that the laser annealed Cu-Ag ion exchanged samples resulted in the formation core shell structure of Cu coated Ag nanoclusters embedded in soda-lime glass and are not simply Cu and Ag nanoclusters scattered inside the dielectric medium.
Fig. 3.34. Experimentally recorded optical absorption spectra of Cu-Ag (Ag core/ 
Cu shell) sequential ion exchanged soda-lime glasses with different laser 
exposure timings

3.13. SILVER COATED COPPER NANOCLUSTERS EMBEDDED IN THE 
SODA-LIME GLASS (Cu CORE AND Ag SHELL)

Silver coated copper (Ag-Cu) nanoclusters were prepared by sequentially ion 
exchanged as detailed before but first dipped in silver bath and then in copper bath for 
copper ion exchange. The as exchanged samples exhibited similar spectra (Fig. 3.30) 
to the case of the Cu-Ag ion exchanged one with only one peak due to copper clusters.

But the post annealing of the ion exchanged samples resulted in an interesting 
phenomenon of evolution of silver peak with the dissolution of the copper peak. This is 
because during annealing the scattered silver atoms start clustering, at the cost of the 
already formed copper clusters resulting in the dissolution of them. The dissolved 
copper clusters are infused by the clustering silver atoms to form the silver coated 
copper nanoclusters inside the glass matrix as seen in the case of copper coated silver 
nanoclusters. This kind of absorption band is accredited the silver coated copper 
nanoclusters as reported earlier [46].
A comparative plot of the experimentally recorded and theoretically calculated optical absorption spectra of the silver coated copper (Ag-Cu) nanoclusters embedded in soda-lime glass is shown in Fig. 3.35. The shape of the spectra matched well with the theoretically calculated spectra confirming the presence of embedded silver coated copper nanoclusters in soda-lime glass.

![Absorption Spectra Graph](image)

**Fig. 3.35.** Experimentally recorded and theoretically calculated optical absorption spectra of Ag-Cu (Cu core and Ag shell) sequential ion exchanged soda-lime glass

**a) Silver coated copper (Ag-Cu) nanocluster embedded in soda-lime glass (constant Ag core different Cu shell thickness)**

The dependency of the absorption spectra on the thickness of the coated material, the theoretical spectra were simulated using Mie theory by keeping the core size is constant and varying the shell (thickness) size or embedded silver coated copper nanoclusters and is shown in Fig. 3.36.
The absorption spectra of silver coated copper (Ag-Cu) or copper core with various silver shell thickness shown in the Fig. 3.36. It is observed from the graphs that the insignificant change is the shape of the absorption bands with increase in silver coat thickness supports well the experimental results, thus disclosing the applicability and reliability of the equation (3.30).

The simulated spectra have sharp peak for Ag cluster alone no significance for Cu cluster for silver coated copper nanocluster (Ag-Cu). The intensity of simulated absorption spectra increases with increasing the thickness of shell (silver thickness).

![Fig. 3.36. Theoretically simulated absorption spectra for Ag-Cu (constant Cu core of different Ag shell thickness) sequential ion exchanged soda-lime glasses](image)
b) Silver coated Copper (Ag-Cu) nanocluster embedded in soda-lime glass - furnace annealed

Experimentally recorded optical absorption spectra for Cu core Ag shell of (Ag-Cu) different temperature annealed samples are shown in Fig. 3.37. From the spectra there is no significant change in shape of the absorption spectra was observed for different temperature annealed samples.

Fig. 3.37. Experimentally recorded optical absorption spectra of Ag-Cu (Cu core Ag Shell) sequential ion exchanged soda-lime glasses with different temperature annealed

This was very well observed from the theoretically calculated spectra also (Fig. 3.36) which show the copper cores coated with silver shells of different thickness embedded in soda-lime glass. The spectra of both the figures exhibited peak centered around at 420 nm only with no signature of copper peaks as seen in the case of copper coated silver nanoclusters. This kind of absorption band is attributed the silver coated copper nanoclusters as reported earlier [46].
c) Silver coated copper (Ag-Cu) nanocluster embedded in soda-lime glasses (Cu core Ag shell) - laser annealed samples

The experimentally recorded optical absorption spectra for (Ag-Cu) or Cu core of Ag shell of various laser annealed timings samples as shown in Fig. 3.38. The spectra show only one broad peak centered at 425 nm. This kind peaks appear only the Ag coated Cu nanoclusters inside the soda-lime glass as reported earlier [17]. But in the case of 500 ms laser annealed sample shows broad peak at 425 nm and slight hump centered at 575 nm, this clearly shows that the silver and copper nanocluster embedded in the soda-lime glass. No significant variation in peak positions is observed for the different exposure timings.

![Image](Image.png)

**Fig. 3.38.** Experimentally recorded optical absorption spectra of Ag-Cu (Cu core Ag shell) sequential ion exchanged soda-lime glasses with different laser exposure timings
The reason for the presence of significant broad silver peaks alone is because on laser annealed Ag-Cu ion exchanged samples resulted in an interesting phenomenon of growth of silver clusters with the dissolution of the already formed copper clusters as the scattered silver atoms start clustering at the cost of the already formed copper clusters resulting in the dissolution of them. The dissolved copper clusters are impregnated by the clustering silver atoms to form the Ag coated Cu nanoclusters inside the dielectric matrix.

Thus embedded bimetallic nanoclusters Cu-Ag (Cu coated Ag) and Ag-Cu (Ag coated Cu) nanoclusters were formed in soda-lime glass by commercial sequential ion exchange technique followed by furnace annealed with different temperatures and laser annealed with different exposures time. The presence of the core shell structures were also confirmed from their respective optical absorption spectra.
REFERENCES


