CHAPTER 4

Dielectric and AC conductivity studies of Ag\(^+\) nanoparticles/Ho\(^{3+}\) doped sol-gel silica matrices

Abstract

The effect of silver nanoparticle codoping on the dielectric properties of holmium doped silica glasses was studied. Silver nanoparticles of size ranging between 20-22nm were produced by the sol-gel technique. One of the samples showed an icosahedral morphology of the nanocrystal formed along with spherical morphology. It was found that the tuning of the dielectric constant values could be accomplished by co-doping. The sample with 1 wt% of holmium has low dielectric constant values within the range 100Hz to 3 MHz due to the formation of quasimolecular structures of holmium. This effect was evaded to some extent with silver codoping as a result of the interdispersion of holmium complexes. Also it was found that the codoping produced a higher dielectric loss which was calculated from the tan δ - log (f) graph. The cole-cole parameters and the Jonscher power law parameters were also calculated and are presented.
4.1. Introduction

Glasses are generally classified as materials with moderate dielectric constants. Several studies have been conducted demonstrating the variation of dielectric constant values in glasses by introducing various rare-earth ions, transition metal ions, semiconductor nanoparticles, metal nanoparticles etc[1-6]. In this chapter we will be discussing on the effect of codoping silver nanoparticle with holmium doped silica glass. The rare earth ions incorporated into amorphous glassy matrix can be accommodated in molecular complexes, quasi-molecular complexes, network modifiers etc. It was found that for rare earth doping concentration ~1mol% the quasi-molecular complexes prevails and the ions are coordinated to non bridging oxygens which are attached to the glass network on one end. Earlier reports on silicate, phosphate, tellurite and borate glassy matrices showed such quasi molecular complexes which discuss the effect on their dielectric and conductivity behaviours [5,6]. In an earlier report Ravindran et.al.[7] studied the effect of silver nanoparticles embedded in aluminium oxide and demonstrated an enhancement in the permittivity due to the presence of nanoparticles. The space charge accumulation at the Ag nanoparticle: dielectric interface and the dipole polarization component were discussed to be the contributing factors. Also the silver nanoparticles were reported to behave like induced dipoles with a frequency dependent response to the small signal.

In this work we co-doped silver nanoparticles into holmium doped silica glass with an intention of tailoring the dielectric
Dielectric and AC conductivity studies of Ag\(^+\) nanoparticles/Ho\(^{3+}\) properties. Here the prime objective is to utilize the dielectric effects due to the presence of holmium and silver nanoparticles as discussed in the introductory paragraph. The samples were prepared via sol-gel process. Samples with and without silver nanoparticle co-doping were produced for a better evaluation.

### 4.2. Experimental

Four samples were prepared with the following composition:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 0.5 Ho</td>
<td>Ho 0.5wt%</td>
</tr>
<tr>
<td>Sample 1Ho</td>
<td>Ho 1wt%</td>
</tr>
<tr>
<td>Sample 0.5 Ho + Ag</td>
<td>Ho 0.5wt% + Ag 0.25wt%</td>
</tr>
<tr>
<td>Sample 1Ho + Ag</td>
<td>Ho 1wt% + Ag 0.25wt%</td>
</tr>
</tbody>
</table>

Tetraethylorthosilicate (TEOS) was used as the precursor for the base silica glass. Water was used for the hydrolysis and ethanol as the solvent. Holmium nitrate and silver nitrate were used for doping the required amount of ions into the silica matrix. These two chemicals were dissolved in water and added to the TEOS+H\(_2\)O+ethanol mixture. The final mixture was stirred for 30 minutes to ensure the homogeneity of the solution before casting. The solvent was cast into polypropylene containers and sealed and kept undisturbed in a dark place for several days for the formation of the gel. Later the gel was heat treated to 600°C in a programmable furnace operating at a heating rate of 1°C/minute.

The samples were characterized using a spectrophotometer (Shimadzu – UVPC 2401), transmission electron microscope (FEI
4.3. Results and Discussion

4.3.1 Optical and structural studies

The absorption spectra of the heat treated sample with (black) and without (red) silver co-doping is shown in Figure 4.1.

The inset figure shows various peaks of Holmium obtained for the silver co-doped sample and the peaks are assigned as the transition from the ground level $^5I_{8}$[8]. For the sample codoped with silver, the
broad peak around 300-350nm could be due to the energy discretization at the absorption edge due to the production of nanocrystals [9]. Thus one infers that Ag nanoparticles cause the peak to appear.

The amorphous nature of the Ho$^{3+}$ alone doped sample was proved by taking the XRD spectrum of the sample as shown in Figure 4.2(a). Figure 4.2 (b) shows the XRD spectra of the samples co-doped with silver.

Figure 4.2 (a) X-ray diffraction pattern of Ho$^{3+}$ in sol-gel silica
Figure 4.2(b): XRD spectra for silver doped samples in comparison with the JCPDS data

The peaks are identified to be arising from the nanocrystals of silver. The assignments of the peaks were done with the JCPDS card number 04-0783. The crystallite size ($t$) was calculated from XRD spectrum using the well known Debye-Scherrer formula [10].

$$t = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} 4.1

where $\beta$ is the measured FWHM, $\theta$ is the Bragg angle of diffraction peak, $\lambda$ is the X-ray wavelength. The sizes of the crystals were 20nm for 0.5Ho+Ag sample and 22nm for 1Ho+Ag sample. Since the nanocrystals are embedded in a silica matrix with holmium doping, possibility of some strain could not be ruled out hence we apply a
modified equation\[11,12\] to evaluate the effective crystallite size. The equation is given by:

\[
\beta \cos \theta / \lambda = 1/\varepsilon + \eta \sin \theta / \lambda
\]

Here, \( \varepsilon \) is the effective particle size and \( \eta \) is the effective strain. The effective particle sizes were estimated to be 21.2\,\text{nm} and 22.9\,\text{nm} for 0.5\,\text{Ho + Ag} and 1\,\text{Ho + Ag} samples respectively. These values are very close to those obtained from the XRD data without applying the Williamson-Hall correction.

Figure 4. 3(a) Transmission electron microscope image of 0.5Ho+Ag.  
**Inset-1:** The corresponding electron diffraction pattern  
**Inset-2:** The corresponding particle size distribution
To confirm the crystallite size the transmission electron microscopy was taken and the values were found to be 20nm for 0.5Ho + Ag and 22nm for 1Ho + Ag and is in well agreement with the values calculated using the Debye-Scherrer formula. Figures 4.3a and 4.3b show the TEM images obtained for sample 0.5Ho+Ag and 1Ho+Ag. The inset of the images shows the electron diffraction pattern and the crystallite size distribution of the respective samples. The size distribution for both the samples were found in the range of
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15 to 35nm, of which the 0.5Ho+Ag sample shows the major size distribution from 20 to 30nm while 1Ho+Ag sample has a comparatively narrow size distribution pattern. The electron diffraction pattern inset shows that 1Ho+Ag sample has a better crystallinity compared to 0.5Ho+Ag sample. The growth of particle size of silver in silica matrix depends mainly on the diffusion coefficient and activation energy of coalescence and more specifically on the heat treatment time and temperature of the matrix [13]. More TEM images of various scales and resolutions are added in the appendix section of the thesis.

Thus it is quite evident that only spherical morphology is observed for 1Ho+Ag sample [14], while for the 0.5Ho+Ag sample multi-twinned particles (MTP) with icosahedral morphology was also seen with in the cluster regime as reported in detail by Anne et.al [15]. Marks has reported in a review article [16] that these MTP structures coexist with fcc structures with in a sample. In a mixture of such structures the icosahedral components may not clearly distinguish itself, because the XRD profile will mostly appear in the same regions where the fcc peaks occur [17]. Also this coincidence of the diffraction profiles get aggravated by a distribution of size of the particles

4.3.2 Dielectric studies

The real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constant of all the samples are shown in Figure 4.4a and 4.4b respectively.
As seen from the Figure 4.4a the dielectric constant varies substantially with the frequency, for low holmium content, upto 10kHz, whereas for the samples containing higher holmium content (1Ho and 1Ho+Ag), the rate of change is almost a constant within the range 1 kHz to 3MHz. On a careful analysis of the slopes, upto 100kHz, of the samples 0.5Ho and 0.5Ho+Ag, it could be understood that the dielectric constant value of the latter decreases at a slower rate which could be attributed to the contribution from the induced dipole like behavior of silver nanoparticles in the low frequency regime[18]. The value of dielectric constant remains almost constant beyond 100 kHz for 0.5Ho and 0.5Ho+Ag and the small enhancement in the permittivity value for the sample 0.5Ho+Ag is due to the presence of nanocrystals as reported earlier [7].
Samples with 1wt% of holmium have a much lower dielectric constant value for the entire range of frequency. The effect due to the formation of quasimolecular structures of holmium shows some predominance in the nanoparticle codoped samples. Also the reduction in the value could be considered due to the interdispersion of the holmium complexes within the matrix diminishing the interaction of silver nanoparticle dipoles. From the trend of the dielectric values from Figure 4.4(a) a tuning of dielectric values could be possible with the silver nanoparticle co-doping.

Figure 4.4b shows the variation of the imaginary part of the dielectric constant ($\varepsilon''$) with frequency.

**Figure 4.4(b):** Imaginary part of the dielectric constant of all the samples.
For samples without co-doping an almost flat response is observed from 3 kHz onwards, whereas with silver co-doping the response is still active for one more order. At moderate frequencies \( \varepsilon'' \) is due to the contribution of ions jump, conduction loss of ion migration, and ion polarization loss [19].

Figure 4.5 shows the frequency dependence of the conductivity of the respective samples.

![Graph showing conductivity vs frequency for different samples](image)

**Figure 4.5:** Frequency dependence of the conductivity of all the samples.

All the samples show a weak dependence of frequency and conductivity up to 10 kHz. It shows an upward inclination in the conductivity values with further increase in frequency. Sample 0.5Ho+Ag shows an elevated conductivity of one order high as compared to other samples. Also it is seen that samples when doped
with higher percentage of holmium has low conductivity at high
frequency as compared to 0.5Ho. The formation of quasi-molecular
complexes serves as hopping sites rather than forming defects.
Hence for higher holmium doping the conduction reduces due to the
formation of more complexes. It could be the pairing of low holmium
doping and the presence of silver nanoparticles enhanced the
conductivity to a much higher value.

A convenient formalism to investigate the frequency
dependence of conductivity in a material is based on the power-law
relation proposed by Jonscher equation given by [20-21]

\[
\sigma_T(\omega) = \sigma_0 + A\omega^s
\]

where \(\sigma_T\) is the total conductivity, \(\sigma_0\) is the frequency independent (dc)
conductivity, and the coefficient \(A\) and exponent \(s\) are temperature
and material dependent parameters. The exponent \(s\) can vary very
differently from material to material depending on co-dopant
concentration, temperature etc., but is always such that, in general,
\(0 \leq s \leq 1\). The values of \(\sigma_0, s\) and \(A\), known as power-law parameters
are tabulated in Table 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\sigma_0 \times 10^{-7})</th>
<th>S</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Ho</td>
<td>2.62</td>
<td>0.98</td>
<td>1.89 \times 10^{-13}</td>
</tr>
<tr>
<td>1Ho</td>
<td>0.1</td>
<td>0.99</td>
<td>8.27 \times 10^{-16}</td>
</tr>
<tr>
<td>0.5 Ho + Ag</td>
<td>41.8</td>
<td>0.48</td>
<td>5.9 \times 10^{-9}</td>
</tr>
<tr>
<td>1Ho + Ag</td>
<td>1.01</td>
<td>0.22</td>
<td>9.4 \times 10^{-9}</td>
</tr>
</tbody>
</table>
Figure 4.6 represents the variation of dielectric loss (tan δ) with frequency. The values of tan δ are found to be decreasing with increasing frequency and attain a constant value at higher frequencies. All the four samples show similar behavior but it can be seen that for the Ho/Ag doped samples, the values of tan δ are found to be lesser compared to the holmium alone doped samples. The low frequency dispersion is due to the space charge effect caused by charge accumulation around the electrodes.
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(a) Imaginary part of impedance vs. real part of impedance for 0.5Ho.

(b) Imaginary part of impedance vs. real part of impedance for 1Ho.
Figure 4.7: (a-d) Real vs imaginary part of the impedance value for all the samples.
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Figure 4.7 depicts the representation of real and imaginary part of the impedance value which interprets the Cole-Cole plot and derives the value of $R_b$, $C_b$ and $\tau$ known as Cole-Cole parameters (Eqns (2)-(5)). It is derived from an equivalent circuit representing the dielectric response of the sample, consisting of an RC element. This ‘RC’ element is characterized by a relaxation time, $\tau$, which is a product of $R$ and $C$.

$$\omega_{\text{max}} R_b C_b = 1.$$ \hspace{1cm} (4.4)

$$\omega_{\text{max}} = \frac{1}{2\pi f_p}.$$ \hspace{1cm} (4.5)

$$C_b = \frac{1}{2\pi f_p R_b}.$$ \hspace{1cm} (4.6)

$$\tau = R_b C_b = \frac{1}{2\pi f_p}.$$ \hspace{1cm} (4.7)

where, $R_b$ is the bulk resistance, $C_b$ the bulk capacitance, $f_p$ the peak frequency and $\tau$ the relaxation time.

Single semicircles are observed for all the samples which can be modelled by an equivalent parallel RC circuit. The peaks of the semicircles are used to determine the relaxation time ($\tau$). The low frequency intercept made by the semicircle on the real impedance axis can be used to determine the dc (frequency independent) resistance of the sample. The values of $R_b$, $C_b$ and $\tau$ are tabulated in Table 4.2.
Table 4.2: Cole-Cole parameters for all the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_b$ (Ω)</th>
<th>$C_b$ (F)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Ho</td>
<td>7.33x10^6</td>
<td>2.17x10^{-11}</td>
<td>1.59 x10^{-4}</td>
</tr>
<tr>
<td>1Ho</td>
<td>1.529x10^8</td>
<td>5.21 x10^{-12}</td>
<td>7.96 x10^{-4}</td>
</tr>
<tr>
<td>0.5 Ho + Ag</td>
<td>5.566x10^4</td>
<td>1.91 x10^{-11}</td>
<td>1.06 x10^{-6}</td>
</tr>
<tr>
<td>1Ho + Ag</td>
<td>2.73x10^6</td>
<td>2.92 x10^{-12}</td>
<td>7.96 x10^{-6}</td>
</tr>
</tbody>
</table>

It can be seen that for holmium alone doped samples $R_b$, and $\tau$ increases with increase in concentration of holmium, while $C_b$ decreases. For the holmium and silver co-doped samples, $R_b$ increases with increase in concentration of holmium. It could be understood that the presence of silver nanoparticles cause a reduction in the relaxation time as well. The polarization process relies on the excitations of trapped electrons from deep levels in the space charge region. Hence the shorter relaxation time $\tau$ in silver doped samples can be accounted due to the presence of excited free carriers in the space charge region which reduces the $R_b$ values as compared to that of the Ho alone doped samples. The presence of spike at low frequencies observed in the semi circles is typical of polarization effects at the electrodes and indicates the presence of an ionic contribution to the electrical conductivity [22-23]. The present work leaves open the possibility of metal nanoparticles embedded glassy media suitable candidates as absorptive glass polarizer, particularly in optical fibre communications. The metal nanoparticle
doped glassy materials can also be employed to actively control light matter interaction which finds application at nanoscale dimensions. Further, closely spaced nanostructures in the form of clusters, arrays or chains may be very useful for transporting optical energy over micrometer scales. They may prove to be promising candidates as optical dielectric polarizers at high optical powers.

4.4. Conclusion

Four samples were prepared with 0.5 wt% and 1 wt% holmium concentrations, two of them were co-doped with silver (0.25wt %). The formation of silver nanocrystals was confirmed by XRD and TEM. Using the Debye-Scherrer formula the crystal size was calculated to be 20nm and 22nm for the sample 0.5 Ho + Ag and 1 Ho + Ag respectively. The TEM images confirm the crystallite size values obtained from XRD.

The dielectric studies conducted on all the samples reveal that the effect of silver co-doping has some effect on the dielectric constant, conductivity and loss tangent values over a frequency range of 10 kHz to 3MHz. A successful tuning of the dielectric constant values can be brought in by the silver co-doping. The sample 0.5Ho+Ag shows a conductivity values which is one order high as compared to the other samples. The low conductivity values for other samples are due to the linking of the quasi-molecular states within the glass matrix rather than the formation of defects. Such defects reduce the hopping conduction by increasing the distance between the hopping sites. The power-law parameters A and s vary considerably for samples with and without silver codoping. From the Cole-Cole
plots it can be inferred that silver codoping has some effects on the $R_b$ and $\tau$ values.

From the above trends and behaviour of the samples over a frequency range from 10kHz to 3MHz the sample with silver codoping could be used as a dielectric material whose dielectric properties could be successfully tuned by controlling the doping concentration of holmium and silver. To sum up, it can be stated that suitable geometrical structures of nanoparticles incorporated in glassy media may open up the possibility of applications in optical energy transport devices, dielectric optical polarizers or photonic materials.

References


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[18] Yuan-Fong Chau and Din Ping Tsai, Optics Communications 269 (2007) 389


