2B.1 Introduction

Nanostructured materials have assumed tremendous importance in recent years because of properties exhibited by them and challenging problems thrown up for providing theoretical explanations [1-4]. The main theme of nanotechnology is miniaturization, the importance of which was pointed out by Feynman [5] as early as 1959 in his often-cited lecture entitled “There is plenty of room at the bottom”. The challenge was to beat Moore law [6] and accommodate 1000 CDs in a wristwatch!. Particularly the materials containing metal nanoparticles are interesting nanoscale systems because of the ease with which they can be synthesized and modified chemically [7]. Metal nanoparticles also offer an advantage over other systems because of their optical (or dielectric) constants resemble those of the bulk metal to exceedingly small dimensions (i.e., < 5 nm). The nanoparticles can be synthesized basically by two methods one is “top down approach” and the other one is called “bottom up approach”[8]. Synthesis of variety of metal nanoparticles in glasses follow the second method, particularly the formation of noble metal nanoparticles inside a glass has been extensively investigated for the past decades because of their excellent properties such as an ultrafast optical response and large third order non-linear susceptibility [9-12]. These kinds of glasses are expected to be promising materials for ultrafast optical switches and optical circuits with micrometer size. Glasses containing metal nanoparticles are also known as photosensitive glasses [13]. Metal nanoparticles precipitated can be utilized to nucleate the crystallites of GC’s [14-16]. It is also reported that the slow relaxation process for non-linear optical response is different for glasses and GC’s due the difference in thermal conductivity between glass and GC’s [10, 17, 18]. Preparation of transparent noble metal
nanoparticles is the most challenging task for researchers in the area of materials science. Further, the fabrication of metal nanoparticles of different size and shape in glass matrix by various methods become the most advanced issue [19-22] Glasses containing metal nanoparticles look very distinctive with different colors [23,24]. Since the quantum size effects and enhanced surface effects are expected to influence the electronic and optical properties at much smaller particle sizes leads more interest for researchers to fabricate the metal nanoparticles in glasses [25, 26, 27]. The investigation on gold ruby glass containing different sized gold nanoparticles is due to their distinctive reddish ruby color [11, 28, 29]. Their structural morphology studies have been done using EXAFS, XRD and XPS methods [30]. Metal nanoparticles in glasses are also precipitated using electron beam, laser and γ-irradiation [28, 31, 32]. In these methods the metal ions are reduced but needs thermal treatment. Electrical conductivity of the ion conducting glasses containing the gold nanoparticles possesses the transition from ionic to electronic conductivity due the polaron hopping which exists in the interface of the glass matrix and the crystallites containing the gold nanoparticles [33]. The dielectric properties of such material show a strong dependence on the individual size of the nanoparticles and their relative spacing within the network [34]. Interestingly the mechanism of dc conduction or dipolar loss is quite different from ionic/electronic conducting glasses. Hence, the glasses with appropriate combination of optical transmission and electrical conductivity are needed for enhancing the performance or introducing new functionality of optoelectronic and solid state ionic devices. Further, a detail studies on current status and future prospects of science and technology of nanomaterials have been reported to show significant and distinct properties of nanomaterials from those of atoms or bulk materials
[35]. The foregoing literature survey suggests that it would be interesting to synthesize Au nanoparticles in glasses and realize characteristic ruby color without adding any reducing agents and heat-treatment. It is well known that the B$_2$O$_3$ is the best glass former and Li$_2$O and BaO are the best network modifiers, and the glasses prepared by these oxides will be more transparent in appearance. Further the Li$^+$ is the good ionic conductor to get the enhanced ionic conductivity in any of the lithium based glasses. Hence, in the present investigations following two glass systems were identified for and potential usage in electronic and optical applications

(i) $30$BaO-$70$B$_2$O$_3$-$x$AuCl$_3$

(ii) $30$Li$_2$O-$70$B$_2$O$_3$-$x$AuCl$_3$

where ‘x’ is the dopant in wt % available in the form of HAuCl$_4$3H$_2$O (Aurochloric acid) which is highly hygroscopic in the open atmosphere.

The samples have been characterized using X-ray diffraction, scanning electron microscopy, electron spin resonance, optical absorption. The samples are optically characterized using UV-VIS optical absorption and Non-linear optical properties using open aperture Z-scan experiment. The prepared lithium-borate samples containing gold nanoparticles are also able to show the mixed conductivity (Li + electron) behaviour and the conductivity studies have been performed at various temperatures over a wide range frequency (100Hz-10MHz).
2B.2 Synthesis of Glass-Ceramic-Nanocomposites Containing Au Nanoparticles.

The base glass with the composition $30\text{BaO}-70\text{B}_2\text{O}_3 - x\text{AuCl}_3$ and $30\text{Li}_2\text{O}-70\text{B}_2\text{O}_3-x\text{AuCl}_3$ (where $x=0.01$, 0.04 and 0.06 wt %) have been prepared by melt quenching technique.

The mixture of the different compositions mentioned above was heated at about 850$^\circ$C for few minutes to homogenize the melt and then raised the temperature to 1000$^\circ$C. Highly homogenous melt was then quenched between two brass plates at room temperature. The quenched glass samples so obtained were found to be ruby-red in color. The deepness of the color was found to be increasing with the increased concentration of gold dopent (Plate 2B.1 and Plate 2B.2).

Table 2B.1: Sample code and chemical compositions of the prepared GCNC’s.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition of network modifier (mol%)</th>
<th>Composition of glass former (mol%)</th>
<th>Dopant (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB-Series</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB (Base glass)</td>
<td>30</td>
<td>70</td>
<td>H\text{AuCl}_4\text{3H}_2\text{O}</td>
</tr>
<tr>
<td>BBA1</td>
<td>30</td>
<td>70</td>
<td>0.01</td>
</tr>
<tr>
<td>BBA2</td>
<td>30</td>
<td>70</td>
<td>0.04</td>
</tr>
<tr>
<td>BBA3</td>
<td>30</td>
<td>70</td>
<td>0.06</td>
</tr>
<tr>
<td>LB-Series</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LB (Base glass)</td>
<td>30</td>
<td>70</td>
<td>H\text{AuCl}_4\text{3H}_2\text{O}</td>
</tr>
<tr>
<td>LBA1</td>
<td>30</td>
<td>70</td>
<td>0.01</td>
</tr>
<tr>
<td>LBA2</td>
<td>30</td>
<td>70</td>
<td>0.04</td>
</tr>
<tr>
<td>LBA3</td>
<td>30</td>
<td>70</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Plate 2B.1: (a) BB, (b) BBA1, (c) BBA2, (d) BBA3 samples
Plate 2B.1: (a) LB, (b) LBA1, (c) LBA2, (d) LBA3 samples
2B.2.1 XRD Analysis

As can be seen in the XRD pattern (Fig. 2B.1), there are no sharp peaks in barium-borate samples, indicates that the percentage of crystallization is very less or the size of the Au particles is too small for reflection. On the other hand, x-ray diffraction pattern of LB and LBA (Fig. 2B.2) show the sharp peaks at 38.71°, 44.87° and 64.95°. These prominent peaks corresponds to reflections from the planes (111), (200) and (220) of gold respectively [19, 36, 37]. It is also noted that the intensities of these peaks increase with the increase of gold concentration. The average gold particle size in the LBA4 sample (0.06 wt% of gold dopant) was calculated using the standard Debye-Scherer equation $D = \frac{K\lambda}{\beta \cos \theta}$.

where $K$ is the particle shape factor (generally taken as 0.9), $\lambda$ is the wavelength of CuKα radiation, $\beta$ is the integral breadth of a reflection (FWHM in radian), and $\theta$ is the Bragg angle at the peak position. The particle sizes were in the order of 28 nm.

![Figure 2B.1: XRD pattern of (a) BB, (b) BBA1, (c) BBA2, (d) BBA3 samples.](image-url)
Figure 2B.2: XRD pattern of (a) LB, (b) LBA1, (c) LBA2, (d) LBA3 samples.

2B.2.2 SEM Analysis

The images for BBA and LBA series with and without gold dopant are presented in Fig. 2B.3 and Fig.2B.4 respectively. One can notice in Fig. 2B.3 (a) and in Fig.2B.4 (a) that the image of the sample (BB and LB) with 0 % of gold dopant shows homogeneous phase, on the other hand the samples with different concentration of gold dopant (BBA and LBA) [Fig. 2B.3 (b) to (d) and Fig. 2B.4 (b) to (d)] clearly show the growth of small crystallites of different size and almost spherical shaped in BBA and almost layered structure in LBA. It is extremely difficult to realize the presence of gold particles in the ‘nano’ range from these images. However, one can conclude that the addition of gold dopant can increase the kinetics of growth of particular phase. Hence the sample containing the micro crystals nucleated by the Au nanoparticles is confirmed by the SEM studies.
Figure 2B.3: SEM of (a) BB, (b) BBA1, (c) BBA2, (d) BBA3 samples
Figure 2B.4: SEM images of (a) LB, (b) LBA1, (c) LBA2, (d) LBA3 samples
**2B.2.3 Electron Spin Resonance Studies**

Electron spin resonance (ESR) studies of the samples have been performed at room temperature using the ESR spectrometer [Model-Expands, Bruker (UK)] to understand the electronic state of the Au in both BBA and LBA samples. It is well known that Au$^{2+}$ are paramagnetic and ESR active. They can form several interesting complexes [38]. On the other hand, Au$^0$ and Au$^+$ is ESR inactive [38, 39]. The ESR spectra of all the samples under investigation are shown in the Fig.2B.5 and Fig.2B.6. It is clearly seen that there is neither sharp signal nor hyperfine split in the entire spectrum, which is indicating that the samples have neither paramagnetic ions nor unpaired electrons. Hence the electronic state of the gold must be either Au$^0$ or Au$^+$ [40]. In a typical ruby glass, before striking the ruby color, gold is dissolved in Au$^+$ state and further, a subsequent heat treatment (with the help of reducing species) gives the striking ruby color. For example, reduction of gold ions with the help of tin as catalyst can be explained by the following redox mechanism [29].

\[
\text{Sn}^{2+} + 2\text{Au}^+ \rightarrow \text{Sn}^{4+} + 2\text{Au}^0 \quad 2B.1
\]

\[
\text{Sn}^{4+} + 2\text{O}^2- \rightarrow \text{Sn}^{4+} + \text{O}_2 \quad 2B.2
\]

Similarly under the electron beam irradiation also the mechanism of reduction of Au$^+$ can be understood as follows,

\[
\text{Au}^+ + e^- \rightarrow \text{Au}^0 \quad 2B.3
\]

The segregation of reduced gold atoms on controlled heat-treatment will form the gold nanoparticles of different size and attributes to the formation of ruby color. But, in the present study, formation of ruby color in BBA and LBA glasses without reducing agent and heat treatment, the mechanism of Au$^+$ to Au$^0$ certainly appears to be
complicated [40]. One of possible mechanisms [41] of reduction of $A^+$ to $Au^0$ is strongly temperature dependent and suspected that during fast quenching from very high temperature (>1000°C) the Au particles may arrest/ agglomerate to form the particles of size <2nm, and the glasses will be colorless because of no surface plasmon (SPR) absorption where as if they are able to agglomerate to form the particles of the size >2 nm the glasses appears to be ruby red in color immediately as it is attributed to the SPR absorption of the visible light in the wavelength range 550-580nm.

Figure 2B.5: ESR spectra of (a) BB, (b) BBA1, (c) BBA2, (d) BBA3.
2B.3 Conclusions

Gold nanoparticles have been synthesized in barium-borate and lithium-borate glasses. The characteristic ruby color has been realized in all the glasses without adding any reducing agent and heat-treatment. This distinct mechanism is suspected to be due to the formation of little bigger size nanoparticles (>2nm) in the as quenched glasses and responds for the surface plasmon resonance to occur in the visible light of wavelength 550-580nm. A morphological change due to the addition of gold dopant has been characterized by XRD and SEM techniques. XRD analysis of BBA GCNC’s does not show any sharp intensity peaks as the barium-borate network is dominating its amorphous nature. The LBA GCNC’s shows the reflection of gold nanoparticles embodied in the lithium-borate network. SEM studies show that the addition of gold
increases the kinetics of growth of the crystallites of different size and shape. ESR studies reveal that the electronic state of gold is either $\text{Au}^0$ or $\text{Au}^+$. 

**Summary:** The synthesized GC and GCNC prepared using thermal treatment have been investigated by various physical techniques namely elastic properties, electron/ion transport and non-linear optical studies. The studies are discussed in the subsequent Chapters of this thesis.
References:


