Comparative Study on Au-Ag composition in Lithium Zinc Calcium Fluroborate Glasses: Nonlinear Optics Perspective

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Abstract. 20Li\textsubscript{2}O-15CaF\textsubscript{2}-20ZnO-45B\textsubscript{2}O\textsubscript{3}-(0.5-X)Au-(0.5-X)Ag, (where X= 0.2, 0.3) glasses were prepared by the conventional melt quench technique and coded as 2G3S and 3G2S respectively. The idea of this current work is to check the compositional dependence on the gold and silver nanoparticles in the glass. The XRD results confirmed presence of Au-Ag (111) peak at 38.11°. The Infrared spectral study confirms the presence of borate segments. The UV Visible Spectroscopic studies confirms the presence of surface plasmon resonance shoulder peak for Ag nanoparticles around 490nm and 509 nm for glass 2G3S and 3G2S which had overlapped with SPR resonance peak of Au around 603 nm for glass 2G3S and around 559nm for glass 3G2S.The nonlinear optical properties were characterized using Z-Scan experimental technique for these glasses and it suggests the Glass 3G2S exhibited better nonlinear refractive index and nonlinear absorption coefficient compared to Glass 2G3S

Keywords: Au/Ag Nanoparticle doped Glasses, Nonlinear optical properties, Z Scan

1. Introduction

Noble metal nanoparticles such as gold, copper and silver exhibit unique feature known as surface plasmon resonance (SPR) which occurs due to the combined oscillation of conduction electrons at the surface of dielectric medium. The SPR and interband transitions of noble metal clusters partially overlaps which leads the electrons in the bands of d and s-p to engage in nonlinear process under SPR resonant condition\cite{1–3}. The nonlinear optics is highly dependent on intensity of incident light and it enables to switch over the applications from optical communications to optical computing depending on its response with light. Nonlinear devices like optical switches and limiters find their application potential in generation of symmetric pulses or compression pulses which results in pulse shaping and
mode locking mechanism. Limiters fit into applications which could expel background noise which improvise the quality of spectroscopic instruments. The optical limiters are known to be used as shields to protect eyes and optical sensors[4–6]. Earlier reports suggest that silver nanoparticle show better nonlinear absorption than gold nanoparticle and hence by tuning the SPR could lead to nano sensors which can be used for biomedical applications[7,8]. The Z-Scan setup is a conventional method for measuring the nonlinear optical properties along with their respective sign convention and the device is highly sensitive compared to other methods as it can also measure the real and imaginary part of susceptibility[9,10]. The preliminary investigation for selecting the host matrix for nonlinearity were reported earlier[11] and on that basis, the work has been further extended to inspect the role of silver composition in higher concentrations of gold nanoparticle doped fluoroborate glasses and for our surprise the transparency and the nonlinear optical properties were relatively better than our previous result. As per our knowledge, there is no report suggesting the choice of Au-Ag dopant concentration responsible for tuning the nonlinear optical properties of Au-Ag nanoparticles doped in glasses.

2. Experimental Details

20Li$_2$O-15CaF$_2$-20ZnO-45B$_2$O$_3$-0.2AuCl$_3$-(0.5-X) Ag, (where X= 0.2, 0.3) glasses of 10 gram batch were synthesized using the conventional melt quench technique. Table 1 is the composition table pertaining to the gold-silver nanoparticles doped glasses. The batches were kept inside muffle furnace and heat treated through step process as mentioned in our previous work[11] and finally the molten glass was quenched at 1050°C on preheated brass molds. The glass samples were annealed for 300°C.

![Figure 1](image1.png)

**Figure 1**: Dichroic behavior of Au doped Lithium Zinc Calcium fluoroborate glasses (2G3Sand 3G2S) prior to transmittance and post transmittance

The glass appears as brown colored glasses but transmit blue indicates that gold and silver nanoparticle has dissolved in the glass leading to dichroic behavior as shown in Figure 1. Further to analyze the optical and structural properties, glass samples were subjected to XRD(PAN-Analytical Xpert 3), FTIR(Perkin-Elmer), UV VIS NIR (Perkin-Elmer lambda75) and Z Scan (Ti: Sapphire Lasers of 800nm, 150 laser pulses fired at a rate of 80MHz) characterization techniques.

| Glass Code | Glass Composition (wt %) |
|------------|--------------------------|
| 2G3S       | 20Li$_2$O-15CaF$_2$-20ZnO-45B$_2$O$_3$-0.2 AuCl$_3$-0.3AgCl |
| 3G2S       | 20Li$_2$O-15CaF$_2$-20ZnO-45B$_2$O$_3$-0.3 AuCl$_3$-0.2AgCl |
3. Results and Discussions

3.1. XRD Results

The XRD pattern as shown in figure 2 confirms that presence the sample is amorphous with its characteristic broad hump between 20°-40° for both the glasses and also exhibits the prominent presence of small hump around 38.11° which is attribute to the (111) FCC lattice of gold or silver nanoparticle in glass[12].

The Miller indices for this peak can be estimated by using Bragg’s equation, 

$$2d_{(hkl)} \sin \theta = n \lambda,$$

where \( \lambda_{Cu} = 0.154 \text{nm} \), ‘d_{hkl}’ is the interplanar distance, and for FCC lattice parameter \( a = 2r\sqrt{2} \), where ‘r’ the atomic radius of gold and silver which incidentally found to be same as 0.144nm[13]. The relationship between ‘a’ and \( d_{(hkl)} = \frac{a}{\sqrt{(h^2+k^2+l^2)}} \) results in estimation of interplanar distance between to Au planes which is found to be 0.2351 nm[11].

3.2. Physical Properties

Physical Properties of glasses were obtained by Archimedes method by immersing toluene and the physical parameters were calculated using the formulae mentioned in reference[14]. Table 2 clearly suggests that incorporation of gold/silver precursor has varied the density but the change with respect to molar volume is not so significant. The values of density in glass 3G2S is higher than 2G3S can be attributed to atomic weight of gold and relatively the concentration of gold is higher in 3G2S. Since the density has increased due to larger concentration of Au-Ag nanoparticles thereby this probably could lead to enhancement of nonlinear optical properties[15] in current glass samples compared to our previously reported[11] result.

Table 2: Structural, optical and physical properties of gold doped Li2O-CaF2-ZnO-B2O3 glasses.

| Structural, Optical & Physical Parameters | 2G3S   | 3G2S   |
|------------------------------------------|-------|-------|
| Density (g/cc)                           | 2.622 | 2.724 |
| Molar Volume (cm3)                       | 37.99 | 36.65 |
| Au Ion Concentration (10+20 atoms/cm3)   | 3.16  | 4.92  |
| Ag Ion Concentration (10+20 atoms/cm3)   | 4.74  | 3.28  |
| Au Interionic Distance (10-9m)           | 1.47  | 1.27  |
| Ag Interionic Distance (10-9m)           | 1.28  | 1.45  |
| Au Polaron Radius(Å)                     | 5.92  | 5.1   |
| Ag Polaron Radius(Å)                     | 5.17  | 5.84  |
3.3. IR Studies

The infrared absorbance spectrum confirms the presence of BO₁ and BO₄ groups as shown in the figure 3 and it is interesting to note that the relative intensity of 3G2S glasses were found to be higher compared to 2G3S, as the results suggest that the presence of higher concentration of Au in glass could probably play a vital role in creating non-bridging oxides which in turn enhances the nonlinear optical property.

The spectrum is categorically divided into five parts viz., borate segments, metallic vibrations and hydroxyl regions as indicated in table 3.

- The presence of peak or IR signals around 400–600 cm⁻¹ confirms the presence of modifying cations like Li⁺/Ca²⁺.
- Around 600 to 800 cm⁻¹ the appearance of second peak or IR signal is attributed to B-O-B bending vibrations.
- The third signal is attributed to symmetric stretching of tetrahedral BO₄ (borate) segment around 800 to 1200cm⁻¹[16]. Since the host matrix contains CaF₂, there could be a probability of existence of distorted Ca₁/₂²⁺ [BO₃/₂F]⁻ tetrahedral group in the same region which might have led to formation of oxyfluoride network in the glasses as reported by Doweidar et al. [17].
- The fourth region indicates the presence of symmetric stretching vibrations of BO₁ (trigonal form) or [BO₂O] groups which are ranged between 1200cm⁻¹ to 1800 cm⁻¹[18].
- Finally, at the higher wavenumber region, the vibrational bands between1700–4000 cm⁻¹ indicates the presence of OH–, water and B-OH [18,19].

![Figure 3: Infrared spectra of 2G3S and 3G2S glasses](image-url)
Table 3: Structural confirmation of Borate segments in Lithium Zinc Calcium fluoroborate glasses.

| Sl. No. | Wave number (cm\(^{-1}\)) | Spectral Assignments                                      |
|--------|---------------------------|----------------------------------------------------------|
| 1.     | 400-620                   | Cationic vibrations of Li\(^+\), Ca\(^{2+}\)              |
| 2.     | 620-780                   | B-O-B bending Vibrations (oxygen linkages between trigonal and tetrahedral borate) |
| 3.     | 780-1170                  | Stretching vibration of BO\(_4\) units, Presence of oxyfluoride network |
| 4.     | 1170-1700                 | Stretching vibrations of BO\(_3\) units                  |
| 5.     | 1700-2000                 | B-OH linkage                                              |

3.4. *UV-Vis-NIR Studies*

The samples exhibit two broad peaks around 490 nm and 509 nm for glass 2G3S and 3G2S respectively can be attributed to Ag nanoparticles which has overlapped with SPR resonance peak of Au around 603 nm for glass 2G3S and around 559 nm for glass 3G2S respectively as shown in figure 4(a). This appears due to surface plasmon resonance and there is a red shift in position for glasses that contains Ag nanoparticles for glasses that contained larger concentration of silver nanoparticle. Similarly the larger concentration of Au nanoparticles have also indicated red shift in its respective SPR positions and the variance in SPR position with composition holds good with references [12,20]. In view of understanding the effect of silver nanoparticles in the Au doped Lithium Zinc Calcium Fluoroborate glasses, the study clearly suggests that the higher concentration of gold nanoparticles in the matrix might lead to red shift of SPR position of Ag nanoparticle to 509 nm and on the contrary the higher concentration of Ag nanoparticles have reduced to 490 nm this could have probably led to overlapping of SPR bands [21].

The direct bandgap and indirect bandgap energy is obtained by extrapolating the plot of \((ahv)\) \(^2\) against energy and the plot \((ahv)^{1/2}\) against energy [11,22]. Figure 4(b) suggests that the direct band gap energy is found to be 3.15 eV for 2G3S and 3.49 eV for 3G2S. The indirect bandgap energy for the glasses was found to be 2.96 eV and 3.25 eV respectively as shown in figure 4(c). The strength of disorderness in the network is estimated by plotting \(ln(a)\) against energy [22] as shown in figure 5(d). The inverse of slope leads to Urbach energy \((E_u)\). The Urbach energy for 2G3S (0.398 eV) and 3G2S (0.418 eV) respectively, indicates that the increase in Urbach energy with the glass doped with higher concentration of gold indicates that there could be probability of creation of more non-bridging oxygens in the network which could enhance the nonlinear optical property and this result correlates with the relative intensities of infrared spectra. It is quite intriguing to note that the lesser concentration of Au/Ag nanoparticles in the matrix undergo red shift which thereby results in increase in nanoparticle size but on the contrary the higher concentration of Au/Ag leads to blue shift which leads to size reduction and hence the size and shape of nanoparticles play a vital role in tuning the nonlinear optical property of glass.
3.5. NLO Studies
The description of the Z-scan experiment setup as mentioned in references [11,15,22,23]. The open aperture data reveals information pertaining to nonlinear absorption and the data was fitted using the equation

\[ T_{OA} = \frac{1}{[1 + \alpha_2 L_{eff}] \left[ I_{00}/\left(1 + (Z/Z_0)^2\right)\right]} \]

Where, \( L_{eff} \) is the effective path length of the sample over the length \( L \) and \( I_{00} \) is laser irradiance intensity.

The closed aperture data was fitted using the equation

\[ T_{CA} = 1 + \frac{4\Delta\varphi_0 \left(Z/Z_0\right)}{\left[1 + \left(Z/Z_0\right)^2\right]\left[9 + \left(Z/Z_0\right)^2\right]} \]
is the Rayleigh Range and it is calculated by \( \frac{\pi \omega_0^2}{\lambda} \), where \( \omega_0 \) is the beam waist and \( \lambda \) is the wavelength of operating laser i.e., 800 nm, \( \phi_0 \) is the phase difference which and it is attributed to nonlinear refraction which is estimated by curve fitting the data from the expression \( \frac{\Delta \phi_0}{2 \pi t_{\text{eff}} \lambda} \) [24].

Figure 5: (a) Closed aperture Z-Scan signature (b) Open aperture Z-scan signature of gold and Silver NPs embedded glasses. Symbols represent the experimental data points. Solid lines are the theoretical fits.

Figure 5(a) is the closed aperture curve which leads to positive nonlinear refractive index \( (n_2>0) \) thereby it exhibits self-focusing nature. The closed aperture data reveals that the incorporation of silver nanoparticle has increased nonlinear refractive indices to \( 4.69 \times 10^{-19} \) m\(^2\)/W and \( 4.92 \times 10^{-19} \) m\(^2\)/W compared to our previously reported work which exhibited \( 4.1 \times 10^{-19} \) m\(^2\)/W [11]. The open aperture data as shown in Figure 5(b) exhibits Reverse Saturable Absorption (RSA) behavior which is due to inter \((d \rightarrow sp)\) and intra band \((sp \rightarrow sp)\) transitions that usually occurs in Au/Ag nanoparticles [15]. The nonlinear absorption coefficient for samples have improvised by incorporation of Au-Ag nanoparticles at relatively much higher concentration in the matrix compared to the previous work. The values of \( \alpha_2 \) for 2G3S is found to be \( 2.19 \times 10^{-11} \) m/W and for 3G2S it is \( 2.44 \times 10^{-11} \) m/W which is quite higher compared to our previous result \( 1.64 \times 10^{-11} \) m/W which was doped only with gold. It is interesting to note that the nonlinear absorption coefficient is found to be higher for the samples with higher concentration of Au (3G2S) compared with higher concentration Ag(2G3S). This indicates that the concentration of Au in Lithium Zinc Fluoroborate matrix enhances the nonlinear absorption coefficient which is attributed to increase in density of glass matrix which could possibly be a reason that either it has led to increase in Au ion concentration [24] and would have possibly agglomerated to enhance the nonlinear absorption coefficient or the blue shift of Au SPR could have led to size confinement effect which could have possibly resulted in enhancing the nonlinear absorption coefficient [25].

\[
F = \frac{2\alpha_2}{n_2 \lambda}
\]

The figure of merit for all the glasses is found to be greater than one and hence these glasses are potential for limiting applications. The factors that could be responsible for tuning the nonlinear optical properties might probably be due to either size or geometry of nanoparticle that is embedded in the glass matrix. Since the glass is dichroic in nature, the shape of nanoparticle could probably be elliptical as reported in [11,12,20]. Thus, further elucidation on geometry could lead pathway for
understanding the compositional effect of Au-Ag nanoparticles in lithium zinc calcium fluoroborate glasses.

4. Conclusion
20Li$_2$O-15CaF$_2$-20ZnO-45B$_2$O$_3$-0.XAu-(0.5-X)Ag, (where X = 0.2, 0.3, coded as 2G3S and 3G2S respectively,) and glasses were prepared by the conventional melt quench technique and it is interesting to note that both glasses exhibited their characteristic SPR of Ag at 490 and 509 nm respectively and SPR of Au at 603 and 559 nm respectively. The glass that contained higher concentrations of Ag/Au exhibited blue shift and on the contrary the compensating lower Au/Ag exhibited red shift, thereby leading to change in size and shape of nanoparticle that could tune the nonlinear optical property. It is observed that 3G2S exhibited higher nonlinear optical property which could be attributed either to increase in density as there is increase in ion concentration of Au atoms or the increase in Urbach energy indicates that the more disorderness in the network which eventually enhances the nonlinear optical property.

Acknowledgement:
The authors AJ and RRK are grateful to Dr. A.H. Rama Rao, President, NES of Karnataka, Dr. S.N. Nagaraja Reddy, Secretary, NES of Karnataka Dr. B.R. Parineetha, Principal, The National College Jayanagar and Dr. N.G. Pramod, Coordinator for Department of Physics (P.G.), The National College Jayanagar (NCJ) for facilitating glass synthesis. The authors are indebted to Dr. Soma Venugopal Rao, Professor, Advanced Centre of Research in High Energy Materials (ARCHEM), University of Hyderabad, Hyderabad-46, Telangana for facilitating Z-Scan experiments. Author AJ is thankful to Mr. Vinayak Pattar, Hall of Science, JNCASR for his qualitative inputs, suggestion and helping in analyzing the results of XRD, UV and IR Spectroscopy.

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