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Effect of SnO_2 and SeO_2 in Non-linear optical properties of Au nanoparticle doped self-striking red ruby glasses

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Abstract

Gold nanoparticle doped self-striking hybrid silicate glasses were prepared by conventional melt quenching technique. Absorption spectra show surface plasmon peak ~527 for $70.95SiO_2$-$11Na_2O$-$9CaO$-$9K_2O$-$0.05Au$ glass and ~517 nm for $70.475SiO_2$-$11Na_2O$-$9CaO$-$9K_2O$-$0.005SeO_2$-$0.5SnO_2$-$0.02Au$ glass. Incorporation of Sn and Se in low concentration shows blue shift in surface plasmon resonance peaks due to their size dependent property as well as creation of NBO's in the silicate network. The enhancement of nonlinear absorption coefficient leading to two photon absorption has been correlated with size dependent in the network due to presence of SnO_2+SeO_2. Glasses doped with low concentration of SnO_2 and SeO_2 show higher nonlinear absorption coefficient β value for limiting and switching device applications.

Keywords: Self-striking AuNp glasses, Two photon absorption, Reverse Saturable Absorbers

1. Introduction

The art of doping gold in glasses has been a practice since roman empire. Understanding "purple of cassius" that emits striking ruby red color due to surface plasmon resonance (SPR) had been key interest for science men working in field of plasmonics. The use of metal nanoparticles (MNP) in the non-linear optics domain elicit great attention for researchers, since plasmonic optical properties of gold nanoparticles are due to electromagnetic field induced by collective oscillations of surface plasmons [1-2] yields good nonlinear coefficients at SPR region which is essential for nonlinear device fabrications. Improvisation of nonlinear refraction of the material leads to improvement of third order nonlinear (TONL) optical property of the material [3]. The applicability of glasses in lasers, waveguides have been focus area for the past two decades, in understanding their saturable absorbers (SA) and reverse saturable absorber (RSA) behavior as it enables to check mode locking, Q-switching in pulsed laser cavity, optical limiting applications and so on [2,4]. The fabrication of nanoscale photonic devices has been uplifted as a contribution of nonlinear optical properties for quick phased in growth design of nanomaterials. These materials have great scientific significance as the applications of nonlinear optics in various fields viz., laser technology, optical computing and data storage, communication, information and image processing [5]. In recent times, the usage of gold nanoparticles have been more as they find themselves apt in especially in segments like biosensors, biocompatible materials. The conjunction of plasmonics in photodynamic therapy is a thrust area to explore as the noble metal nanoparticles are less toxic in nature with strongly enhanced localized SPR [6]. Tailoring the NLO coefficients and SPR that exhibit strong nonlinear absorption can be used in either bio imaging applications or optical limiters. Nonlinear absorption can be tuned to result in SA or RSA behavior. It is

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evident that NLO properties have strong wavelength dependence and pulse duration as the coefficients of nonlinear refractive index and absorption depends on intensity of light, therefore it is very important to check for nonlinear properties over a wide- range of wavelength [7]. The gold nanoparticle that exhibit optical limiter applications have potential application in protection of eyes from highly intense laser radiation [8]. Wavelength-dependent investigation determines necessary validation about the resonance effects observed. The present research work focuses on NLO properties of gold NPs embedded in hybrid silicate glasses at visible region (532 nm, excitation) and discuss the observed change in optical nonlinearities on these glasses. investigated.

2. Experimental details

70.95SiO_2-11Na_2O - 9CaO - 9K_2O - 0.05Au (Sample Code: 0Se:0Sn:5Au), 70.475SiO_2-11Na_2O-9CaO-9K_2O-0.005SeO_2-0.5SnO_2-0.02Au (Sample Code: 5Se:5Sn:2Au). Precursors for the glasses were 99.9% pure finely powder analytical grade SiO_2, Na_2O, CaO, K_2O,SnO_2, and Au Nanoparticles solution (Prime Co. LTD, 8-20 nm size). The whole of composite were mixed and filled in a high purity alumina crucible (each batch weighing about 30 g). The powder was melted at 1500˚C by an electrical furnace and after melting, the melts were quenched in air using a preheated stainless steel mould. The quenched glasses were annealed at 600˚C for 3 hour for reduce thermal stress, and cooled down to room temperature. Finally, all glass samples were cut and then finely polished to a dimension of 0.3cm x 0.5cm x 1.0cm for further investigation.

The density were measured by Archimedes principle method. Refractive index measurement were obtained from Abbe's refractometer (ATAGO) with sodium vapor lamp that provide light of wavelength of 598.3 nm (D line) and mono bromonaphthalene as a contact liquid. The UV-Visible spectrophotometer (Cary-50) was used to measure optical spectra of glass samples. Open aperture Z-Scan measurements were calculated using HOLMARC (Model: HO-ED-LOE-03) setup.

3. Results and discussion

3.1 Physical Parameters

Density of glasses were determined using Archimedes principle and interestingly it is found that there is a decrease in density by incorporation of selenium and tin in the matrix as a result the field strength for these glasses were found low. As the gold concentration was reduced to 0.02 mol%, the ion concentration was found to decrease and as a result the polaron radius for this glass is slightly higher compared to 0.05 mol% of Au. The refractive indices of these glasses were determined using Abbe refractometer, for which the glasses containing 0.02 mol% Au was found to exhibit lesser value compared to 0.05 mol% of Au. It is interesting to note that, the incorporation of selenium and tin in the matrix has reduced the density of glass and there is a change in refractive index of glasses, such changes are quite possible when more polarizing species present in the glass system. In the present case the glass show more polarizing species in 5Se:5Sn:2Au glass due to presence of Sn^{4+} and Se^{4+} ions as explained by the possible oxidation reaction below. This may be due to higher ionic refraction of Sn^{2+} and Se^{4+} that allow the network to be deformable and polarizable [9].

$$2Au^0 + SnO_2 + SeO_2 \rightarrow Au_2O + Sn^{4+} + Se^{4+} + {}^3/_2O_2 \uparrow \quad (1)$$

$$Sn^{4+} + Se^{4+} + 4Au^0 \rightarrow Sn^{2+} + Se^{2+} + 4Au^+ \quad (2)$$

$$SnO_2 + SeO_2 + 8AuO \rightarrow Sn^{4+}O_6^{2-} + Se^{4+}O_6^{2-} + 8Au^0 \quad (3)$$

3.2 Optical Properties

The synthesized glass samples were self-striking ruby in color as displayed in Fig. 1, when doped with Au nanoparticle and also when doped with SeO_2 and Sn_2O contents in glass matrix observed same color. UV absorption spectra were analyzed as depicted in Fig. 2. The samples present a broad SPR absorption band centered at ~520 nm, and this occurrence of SPR peak is attributed to the band-to-band transition in Au-NPs (i.e., from the 'd' band to the s–p conduction band of the Au-NPs). The apparent size of nanoparticle of these glasses can be estimated using the formula [3].

$$r = \frac{Av_f}{2\pi c\left(\frac{\Delta\lambda}{\lambda^2{}_{SPR}}\right)} \quad (1)$$

Where, A =1.2, V_f is the Fermi velocity of gold for bulk medium i.e., 13.82×10^5 m/s, c is speed of light in vacuum, $\Delta\lambda$ is full width half maximum (FWHM) and $\lambda^2{}_{SPR}$ is the SPR wavelength. The above theoretical model for estimation of size of nanoparticle is valid for spherical nanoparticles and for size of nanoparticles lesser than the mean freepath of electrons in bulk metal i.e., lesser than 37.7 nm. It is clearly evident that, the broaden shoulder spectra of 2Au would have lesser size of nanoparticles compared to sharp Gaussian peak of 5Au as the FWHM is lesser for the latter. This can also be correlated as the ion concentration for the former glass is lesser than that of latter. There is a blue shift of SPR positions from the former glass which is confirmed by reduction in Au-NP density as well as the decrease in size of nanoparticle[10]. In our previous work, Ruangtaweep et.al., reported that the incorporation of SeO_2 has decreased the size of AuNp due to more agglomeration of Au nanoparticles and as a result due to confinement of gold nanoparticles, the SPR peak shifts towards the shorter wavelength. [11].

The linear absorption coefficient of these glasses were calculated using the relation,

$$\alpha(\lambda) = 2.303\left(\frac{A}{t}\right) \quad (2)$$

Where, A and t, are the absorbance and thickness of the glass, on basis of electronic structure of the optical absorption edge in glasses can be evaluated by the following expression

$$\alpha h\nu = B'(h\nu - E_{opt})^m \quad (3)$$

Where α is linear absorption coefficient, B' band tailing parameters, E_{opt} is optical band gap energy. The index m refers to the type of transition of electrons that hops from valence band to conduction band. If the hopping of electrons between the bands occur along the same momentum, then index m = 2, accounts for direct band gap. While the electrons between the bands hop on to the some other momentum space, then index m= ½ which can be accounted for indirect band gap. The tail of energy in optical absorption spectra when plotted against $(\alpha h\nu)^{1/2}$ or $(\alpha h\nu)^2$ reveals the direct band gap and the former reveals the indirect band gap energy. It was also found that the direct band gap and indirect band gap energy for the latter

Table 1.

Physical Parameters	0Sn-0Se-5Au	5Sn-5Se-2Au
Density (g/cc)	2.526	2.5142
Molar Volume	24.967	25.362
Refractive Index	1.5224	1.5087
Ion Concentration (Au) 10^{18} ions/cm^{-3}	2.37576	9.35481
Polaron Radius (nm)	3.07738	4.19729
Field Strength (10^{19}cm^{-2})	2.07984	1.11803

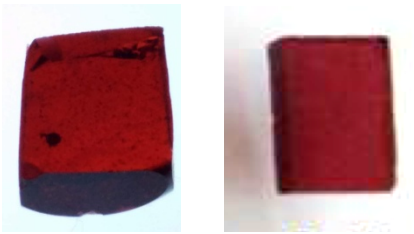

Fig. 1. Au doped self-striking red glass Sample Code: 0Se:0Sn:5Au (left) and Sample Code: 5Se:5Sn:2Au (right).

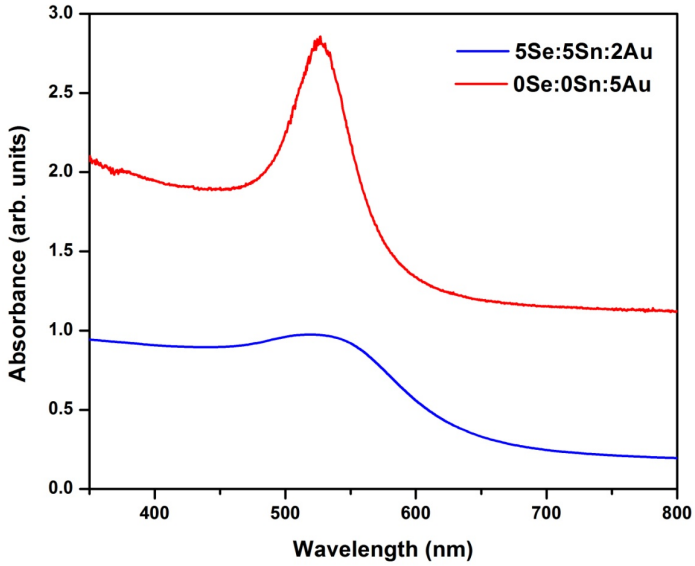

Fig. 2 Absorption spectra 0Se:0Sn:5Au and 5Se:5Sn:2Au glass samples.

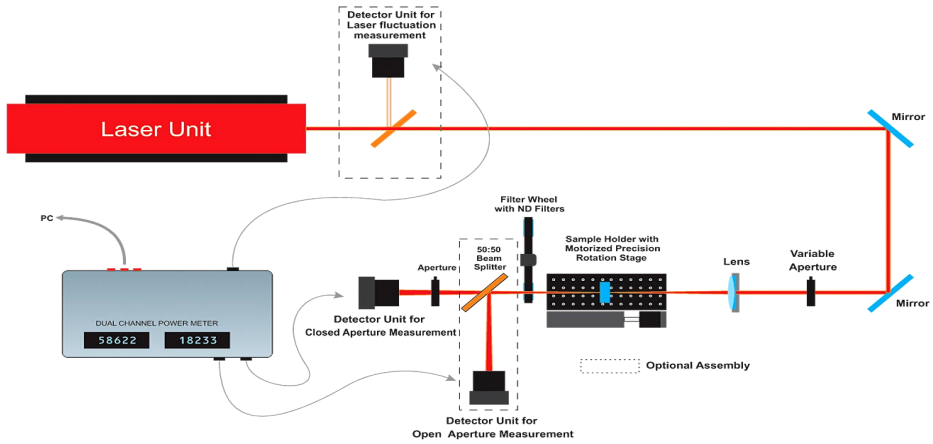

Fig. 3 Block diagram of the Z-Scan apparatus.

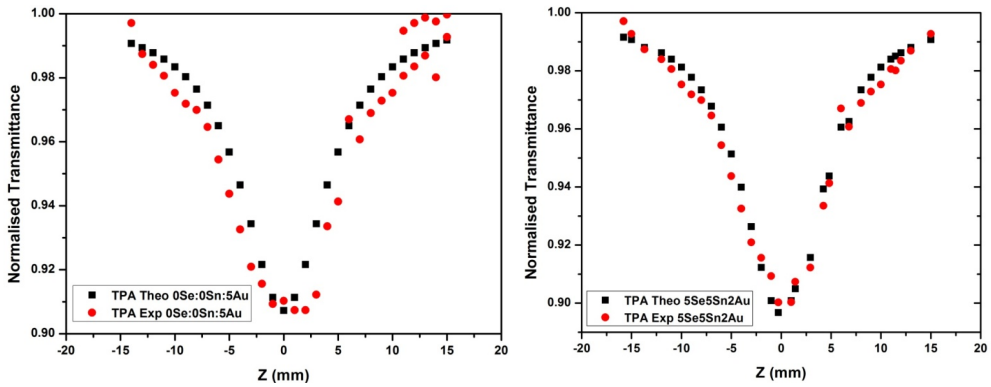

Fig. 4 Open aperture Z-Scan measurements for 0Sn-0Se-5Au and 5Sn-5Se-2Au.

is found to be lesser than the former as reported in table 2. It can be concluded that the effect of Sn in lower concentrations have resulted in polarizing Au atoms in Silicate matrix and thus leading to blue shift in the spectra.

3.3 Nonlinear optical properties:

Open-aperture Z-scan measurements were performed for determining the nonlinear absorption coefficient of the nanocomposite samples. Figure.3 depicts the block diagram of the instrument used for obtaining nonlinear optical properties. In our experiment, we used DPSS laser unit emitting at the wavelength of 532 nm(2.33 eV). Samples of 3 mm thickness were loaded on a programmable linear translation stage. The laser beam was focused using a plano convex lens and the sample was translated along the beam axis (z-axis) through the focal regime. The input energy reaching the sample and the energy transmitted by the sample were measured using two Si photodiodes. In the Z-scan experiment, at each z position the sample experiences different laser intensity and thus an intensity dependent transmittance of the sample can be obtained from this measurement. The z-scan measurements were automated using Holmarc software and the data was recorded for different Z positions.

Z-scan experiments were performed using solid state laser of 532nm as a probing source. The intensity profile has fundamental transverse Gaussian mode can be focused into the most concentrated spot, as it obtains the maximum intensity of the laser at the z-point or focus point (i.e. z=0) . The beam waist radius of a spatial beam profile with the circular cross sections for all the possible values of z can be calculated by using the following equation,

$$\omega(z) = \omega_0 [1 + (Z/Z_0)] \quad (4)$$

where, Z_0 is the Rayleigh range and ω_0 is the beam waist radius at the focus, measured during the z-scan experiment. The nonlinear absorption coefficient β can be obtained by fitting the experimental data of open aperture curve with the equation

$$T(z) = 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}(1 + Z^2/{Z_0}^2)} \quad (5)$$

Where, T(z) is the transmittance, I_0 is the intensity at the focus and L_{eff} is the effective length of the sample.

As from the Fig.4 the open aperture data (experimental) obtained fits well with the above equation (5) (theoretical). Local field enhancement leads to enhancement of nonlinear optical properties in metal nano particles. The SPR of Au NP's are closer to the excitation wavelength of laser that are used for NLO studies that leads to plasmon band bleach as they are indicated in the wings of Z Curves [8]. From Fig.4 both these glasses possess RSA behavior as the intensity of beam decreases leading to inverted Gaussian profile which is due to two photon absorption process that occurs in glasses. This can be attributed due to the mixed intra-band and interband (sp→sp and d→sp, respectively) transitions, as reported earlier by J.Gangareddy et.al [10]. The two photon absorption coefficient (β) for 0Sn-0Se-5Au showed 2.06×10^{-10} m/W and 5Sn-5Se-2Au showed 2.33×10^{-10} m/W suggesting that the addition of SnO_2 and SeO_2 show higher value than undoped glass. The present glass shows higher than other glass systems $60Bi_2O_3$-$30B_2O_3$-$10SiO_2$ (1.0×10^{-10} m/W) [12], BBS glass (2.4×10^{-10} m/W) [13], BBS-Au1 (7.4×10^{-11} m/W) [13], BBS-Au2 (5.1×10^{-11} m/W) [13], Au NP in L1-4 (6.4×10^{-12} m/W) [2], and Au NP in L1-8 (1.8×10^{-11} m/W) [2]. Our results are consistent with other silicate glasses doped with noble metal nanoparticles, which are used for optical limiting properties and photonic devices that control amplitude gain or extinction, polarization, phase, reflection and refraction of light [14] including the protection of human eyes and sensitive optical detectors from accidental exposure to intense light beams.

The glasses containing tin and selenium doped with 0.02 mol% of Au show more nonlinearity as the presence of Se, and Sn participate in creating more number of non bridging

Table 2.

Absorption Studies Parameters	0Sn-0Se-5Au	0.5Sn-0.05Se-2Au
SPR Positions (nm)	527.39	516.94
Direct Band gap (eV)	2.67	2.71
Indirect Band gap (eV)	2.54	2.58
Theoretical Size of Au Nanoparticle (nm)	17.25	8.3

oxygen's and hence there is an increase in nonlinear absorption coefficient. As NBOs are less stable and weakly bound to the network, the valence electrons are easily deformable by the laser electromagnetic field, as a result there is an enhancement in nonlinearities [8,15].

4. Conclusion

It can be concluded that the addition of Sn in the matrix influences in creating the NBO's which leads to reduction in density and as a result the reduction in Au NP concentration. The above observation can be correlated as it has blue shifted SPR peak positions as well as size dependent property. The effect of NBO's created by Sn in this matrix has taken part in enhancing the nonlinear properties. The RSA behaviors possessed by these samples indicate that these glasses have potential use in optical limiters and switching device applications.

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