Antiresonant Interferometric Nonlinear Spectroscopy (ARINS) Study of Metal Nanocluster-Glass Composites.

Binita Ghosh1, Purushottam Chakraborty1, B P Singh2 and T Kundu2

1. Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India
2. Physics Department, Indian Institute of Technology-Bombay, Mumbai 400076, India

E-mail: binita.ghosh@saha.ac.in

Abstract. Linear and nonlinear optical properties of copper and gold nanoclusters in fused silica glasses synthesized by 200 KeV Cu+ and 1.5 MeV Au+ ion implantation at a dose of $3 \times 10^{16}$ ions/cm² have been studied. UV-Vis spectroscopy has revealed prominent linear absorption bands at characteristic surface plasmon resonance (SPR) frequency signifying appreciable formation of copper and gold colloids in glass matrices. Third-order optical properties of the nanocluster-glass composite materials have been studied by Z-Scan and Anti Resonant Interferometric Nonlinear Spectroscopy (ARINS) techniques. The sign of the nonlinear refraction is readily obtained from Z-scan signature. The ARINS technique utilizes the dressing of two unequal-intensity counter-propagating pulsed beams with differential nonlinear phases, which occur upon traversing the sample. This difference in phase manifests itself in the intensity-dependent transmission. The nonlinear refractive index, nonlinear absorption coefficient and the real (and imaginary) parts of the third-order optical susceptibility have been extracted from ARINS data. Results of the investigation of the nonlinear refraction using the above two techniques and the possible mechanisms responsible for the nonlinear optical responses are presented in the current paper.

1. Introduction

There is a considerable interest in finding materials having appreciable optical nonlinearities. Nanomaterials have drawn great attention because of their distinguishable linear and nonlinear optical properties, which differ remarkably from bulk materials. Metal nanoparticles possess interesting optical properties. For example, nanoparticles of alkali metals and noble metals like copper, silver and gold show a broad absorption band in the visible region of the electromagnetic spectrum [1, 2], which is substantially different from the flat absorption of the corresponding bulk metal in this region. The optical absorption spectrum of such materials shows a resonance band, which is due to the surface plasmonic excitation. The metal nanocluster composite glasses (MNCGs) exhibit a resonant third-order optical nonlinearity, which can be enhanced by operating at wavelengths near the Surface Plasmon Resonance (SPR) band of the MNCGs. Glasses possess macroscopic inversion symmetry, allowing only odd-order nonlinearity. Introducing metal nanoclusters in glass matrices can further enhance the third-order nonlinear optical response of the glass matrices. Ion implantation has been shown to produce high-density metal colloids in glasses and other materials [3]. The high precipitate volume fraction and small size of nanoclusters in glasses lead to the generation of third-order susceptibility much greater than those for metal-doped solids [4].
The present work reports a systematic study on the optical properties of Cu$^+$ and Au$^+$ implanted fused silica glasses. We have demonstrated that Cu and Au nanoclusters of various sizes can be safely created in as-implanted silica glass samples; evidenced by the pronounced optical absorption bands. Nonlinear optical measurements of these metal nanocluster-glass composites have been made by Z-Scan and Anti-Resonant Interferometric Nonlinear Spectroscopy (ARINS) techniques and the results of the investigation on the nonlinear refraction and the possible mechanisms responsible for nonlinear responses have been discussed.

**Experiment:**

Optical grade fused silica glass specimens about 1mm thick were used as substrates. Implantation was performed with Au$^+$ ions using 1.7 MeV Tandem Accelerator and for Cu$^+$ ions using a high current isotope separator-cum-ion implanter (Danfysik). The implantation energies were chosen as 200 keV and 1.5 MeV for Cu$^+$ and Au$^+$ ions, respectively with a dose of $3\times10^{16}$ ions/cm$^2$. Following implantation the samples were heat treated at 400$^\circ$C for 1 hour in Ar atmosphere. Rutherford Backscattering Spectrometry (RBS) has been done to study the depth distribution and actual concentration of Au and Cu atoms. The RBS spectra were taken with 2 MeV He$^+$ ions using a surface barrier detector (resolution ~ 15 KeV) kept at an angle of 165$^\circ$. Optical absorption of the implanted samples was measured in the wavelength range 300 – 700 nm using UV-Vis Spectroscopy. Nonlinear optical properties of the implanted samples have been investigated using Z-Scan and Anti-Resonant Interferometric Nonlinear Spectroscopy (ARINS) techniques.

The working principle [5] and the experimental details of the Z-Scan technique were described in our earlier works [6, 7]. The Anti-Resonant Interferometric Nonlinear Spectroscopy (ARINS) technique proposed by Lee and Hughes (LH) [8] is a simple, sensitive, single beam technique based on an anti-resonant ring (Sagnac) interferometer for simultaneously measuring the real and imaginary contributions to optical nonlinearity and it utilizes the dressing of two unequal-intensity counter-propagating pulsed beams with differential nonlinear phases that occur upon traversing the sample. This difference in phase manifests itself in the intensity-dependent transmission. Photo-detection of the transmission of the ARINS yields spatially and temporally integrated response. Figure 1 shows the schematic diagram of ARINS setup. We used a Ti-Sapphire laser of pulse width 70fs-100fs and tunability of 700-850 nm. The repetition rate was 100MHz. A 50-50 beam-splitter divides the incoming pulsed beam into two counter-propagating pulses having a $\pi$ phase difference. The pulses propagating in the clockwise (CW) direction are reflected by an uncoated flat with 6° wedged rear-surface, while those propagating in the counter-clockwise (CCW) direction are reflected by a high-reflectivity mirror.

![Figure 1. Schematic diagram of ARINS setup](image)
Thus this technique is based on the dressing of two unequal intensity counter-propagating pulses. These two pulses again recombine at the beam splitter to yield ARINS transmission, 

\[ |E_{\text{out}}|^2 \propto |E_{cw} + E_{ccw}|^2 \]

where \( E_{cw} \) and \( E_{ccw} \) are the optical fields travelling in clockwise and counter-clockwise directions, respectively. The two counter-propagating fields traversing the ring acquires linear as well as intensity-dependent nonlinear phase shifts. Since both the fields traverse the same optical path through the ring and encounter the same interactions with the optical elements, linear interactions would affect their amplitude and phase in identical manner. For an exactly 50% beam splitter, in absence of any nonlinear interactions, the two returning fields will be having the same amplitude and phase difference between them and consequently, will interfere destructively at the beam splitter to yield zero transmission. In this ‘balanced’ condition all the input power is reflected back to the incident direction. Measurement against this dark background provides the basis for the improved sensitivity essential for measuring relatively weak signals. Any small deviation from the ideal splitting ratio (\( \delta \)) results in a leakage from the ARINS and is responsible for the background that limits the sensitivity of the measurement. If the sample under investigation exhibits nonlinear response, the two unequal intensity counter-propagating pulses will undergo different phase changes after passing through the sample. Their superposition on the beam splitter will result in the intensity-dependent transmission of the ARINS, which is related to the nonlinear response of the sample.

**Results and discussion:**

Figures (2a) and (2b) show the linear optical absorption bands for Au\(^+\) and Cu\(^+\)-implanted glass samples, respectively. As evidenced from the figures the absorption bands appeared at around 490 nm and 580 nm for Au\(^+\) and Cu\(^+\) implanted samples, respectively. Cluster sizes estimated from the Mie theory [9] have been found to be within 3-5 nm in the present cases. These are, however, rough estimates based on the assumption that the clusters are spherical.

**Fig.(2a) Optical absorption spectra of Au\(^+\) sample**  **Fig.(2b) Optical absorption spectra of Cu\(^+\) sample**

In order to study the nonlinear properties of this effective medium, a pulsed light beam with instantaneous electric field strong enough to generate third-order nonlinear effects is allowed to fall onto the sample. Two-photon absorption coefficient given by \( \beta \) is related to the imaginary part of \( \chi^{(3)} \).

\[
\beta = \frac{2\pi}{\lambda n_0^2 \epsilon_0 c} \text{Im}[\chi^{(3)}]
\]

(1)

where \( n_0 \) is the linear refractive index of the material. The nonlinear refractive index of the material is related to the real part of \( \chi^{(3)} \) by the relation [10]
The general form for the electric field of a Gaussian beam is given by

\[ E(Z, r, t) = E_0(t) \exp \left( \frac{-r^2}{w^2(Z)} \right) e^{i \phi(Z, t)} \]  

(3)

where \( E_0(r, t) \) is the incident electric field. For the weaker CW beam, \( \alpha(I) = \alpha \) and \( n(I) = n_0 \).

For the stronger CCW beam, \( \alpha(I) = \alpha + \beta I \) and \( n(I) = n_0 + n_z I \).

The ARINS leakage is given by

\[ \left| E_{out}(r, t) \right|^2 = \left| E_{cw}(r, t) + E_{cw}^*(r, t) \right|^2 \]  

(4)

The measured quantity in this experiment is the transmitted pulse energy

\[ W = 2 n c e_0 \int_{-\infty}^{\infty} \int_{0}^{t} E_{out}^2 2 \pi r dr dt \]  

(5)

Defining \( I_{out} = 2 (\ln 2)^{1/2} W / \pi^{1/2} w^2(Z) \) which has the dimensions of intensity, we get \[8,11\]

\[ I_{out} = 2 n c e_0 R I_{in} \exp(-\alpha L) \times \left[ 4 \delta^2 + \beta L \delta I_{in} + \left( \frac{\beta^2}{16} + \left( \frac{kn_z}{2} \right)^2 \right) L^2 I_{in}^2 \right] \]  

(6)

The ARINS output transmission \( I_{out} \) is a cubic polynomial of incident intensity \( I_{in} \) and the coefficients are directly related to \( \eta_2 \) and \( \beta \), as shown in the expression. In this equation \( \alpha \) is the linear absorption coefficient, \( L \) is the sample thickness, \( R \) is the reflectivity of the low-reflectivity mirror and \( \delta \) represents the small deviation from the ideal splitting ratio of the beam splitter. For \( \delta = 0, I_{out} \propto I_{in}^3 \), in which case the simultaneous evaluation of \( n_z \) and \( \beta \) becomes difficult. However, a small nonzero \( \delta \) makes the analysis much simpler as each term of the polynomial can be evaluated directly. To verify our formulation and demonstrate the application of ARINS, we measured the real and imaginary contribution to the third-order nonlinearity of our samples. As it is clear from the above equation, ARINS cannot give any unique value of the nonlinear parameters (\( \eta_2 \) and \( \beta \)) as far as sign of these parameters are concerned. Z-scan provides us exactly the sign of the parameters \[6,7,12\].

Combining the output of both the experiments we have calculated the values of \( \eta_2 \) and \( \beta \). Figures 3a and 3b show the ARINS data for the Au\(^{+}\) and Cu\(^{+}\) implanted samples, respectively. Observations were carried out at the wavelength of 737.18 nm. The ARINS output shows a clear curvature indicating the nonlinear signature of the samples. The values of the nonlinear parameters are shown in the table below.

| Sample          | \( \eta_2 \) cm\(^2\)/W | \( \beta \) cm/W | Re \( \chi^{(3)} \) | Im \( \chi^{(3)} \) | Abs \( \chi^{(3)} \) |
|-----------------|-------------------------|-----------------|-----------------|------------------|-----------------|
| 1.5MeV Au\(^{+}\) (1×10\(^{17}\)) | -1.45×10\(^{-11}\)   | -2.6×10\(^{-8}\) | 1.457×10\(^{-8}\) | 1.53×10\(^{-10}\) | 1.456×10\(^{-8}\) |
| 200KeV Cu\(^{+}\) (3×10\(^{16}\)) | -3.65×10\(^{-15}\)   | -6.4×10\(^{-12}\) | 3.66×10\(^{-12}\) | 3.74×10\(^{-14}\) | 3.66×10\(^{-12}\) |
In absence of any nonlinearity in the sample, the 2\textsuperscript{nd} and 3\textsuperscript{rd} term in Eq.(6) become zero, reducing the equation to a linear one, which when plotted should give a straight line. Figure 4 shows the linear ARINS output for the fused silica substrate, in parity with the above stated reason. Therefore, it can clearly be stated that nonlinearities in this case arise entirely due to the presence of metal ions within the fused silica substrates.

As the interacting wavelength is far away from the resonance in Au and Cu sample (nonresonant condition), the values of the nonlinear parameters obtained from the ARINS calculation is different from the Z-scan part. Much better and accurate values can be extracted by this ARINS technique once we use the resonant wavelength to pump the sample. This part of the work is still in progress and better results are awaited. However the sign of the nonlinearity remains same in both the cases. The scatter in the z-scan data is about \( \pm 4\% \), which obviously limits the sensitivity of the technique. Considering the beam waist at the focal point (9.95 \( \mu m \)) and peak power (19 kW) of the laser pulse used in the Z-Scan experiment, the peak intensity at the focal point was estimated to be 12 GW/cm\(^2\), which could be relatively strong to produce significant sample heating. This implies that the nonlinearity measured by Z-Scan have a great extent of thermal contribution.
The third-order nonlinear optical response of the present composite material mainly originates from electronic effects in metal nanoclusters. These electronic contributions are due to both intraband and interband transitions. The first one corresponds to transitions within the conduction band and the second one to transitions from the upper levels of the filled $d$ band to the levels above the Fermi level in the conduction band. In the case where the clusters are excited by ultra-short laser pulses, a hot electron phenomenon may superimpose on the pure electronic nonlinear contributions to $\chi^{(3)}$ [13].

Conclusion:
Enhanced nonlinear optical responses have been observed in the MNCGs, synthesized by metal implantation followed by thermal treatments. The sign of the nonlinear absorption and refractive index obtained from Z-Scan measurements have been used in choosing the unique nonlinear parameters extracted from ARINS, enabling us to determine the absolute value of nonlinear susceptibility $\chi^{(3)}$.

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