APPENDIX
NONLINEAR ABSORPTION BY Z-SCAN MEASUREMENT

Optical nonlinearity is defined in a simple way as any deviation from the linear relationship between a material's polarization response and an applied electromagnetic field. The schematic representation of the nonlinear absorption process is shown below.

![Diagram of linear and nonlinear absorption process](image)

**Fig. 1. Schematic representation of linear and nonlinear absorption process**

Before a beam of light impinges on a material all the electrons, atoms and molecules of the material are in the ground state (G). But when the material is irradiated with a light, a transition from the ground state (G) to the first excited state (E1) takes place due to the absorption of energy from the photons. This gives rise to linear absorption. Due to abundance of photons, a further transition from the excited state (E1) to (E2) is accomplished, giving rise to what we call the nonlinear absorption. Dielectrics embedded with nano size metal clusters exhibit large third order nonlinear optical properties like self focusing, intensity dependent index of refraction, optical bistability and third harmonic
generation. In the present work we report the nonlinear absorption of silver nanoclusters embedded in soda-lime glass by the Z-scan technique. In this technique a high intense laser beam is incident on the sample and the intensity of the transmitted light at far field is collected at the detector as a function of the sample position. The theoretical equation predicting the normalized transmittance as a function of the sample position is given below

\[ T(Z) = \frac{\int_{-\infty}^{\infty} P_z(\Delta \Phi(t)) dt}{S \int_{-\infty}^{\infty} P_z(t) dt} \]  

(1)

where \( T(Z) \) is the normalized transmittance as a function of distance \( Z \). The equation is derived as follows:

Considering a Gaussian beam of waist radius \( w_0 \) traveling in \( Z \) direction, we can write \( E \) the peak electric field as

\[ E(z, r, t) = E_0(t) \frac{w_o}{w(z)} \exp\left(-\frac{r^2}{w^2(z)} - \frac{ikr^2}{2R(z)}\right)e^{-i\Phi(r, z)} \]  

(2)

where \( w^2(z) = w_o^2(1 + \frac{z^2}{z_o^2}) \) is the beam radius, \( R(z) = z(1 + \frac{z^2}{z_o^2}) \) is radius of curvature of the wavefront at \( z \), \( z_o = \frac{kw_o^2}{2} \) is the diffraction length of the beam, \( k = \frac{2\pi}{\lambda} \) is the wave vector and \( \lambda \) is the laser wavelength. \( E_0(t) \) is the radiation electric field at the focus and contains temporal envelope of the laser pulse. The term \( e^{-i\Phi(r, z)} \) contains all the radially uniform phase variations. As we are concerned with calculating the radial phase variation \( \Delta \Phi(r) \), the slow varying
envelope approximation (SVEA) applies and all other phase changes that are uniform in \( r \) are ignored. The amplitude and phase of the electric field are governed by the simple equations

\[
\frac{d\Delta\phi}{dz} = \Delta n(I)k \quad (3)
\]

\[
\frac{dl}{dz} = -\alpha(I)l \quad (4)
\]

In the above equations \( z' \) is the propagation depth in the sample and \( \alpha(I) \) includes the linear and nonlinear absorption terms. Solutions of equation (3) and (4) gives the phase shift at the exit of the sample surface which follows the radial variation of the incident irradiation at a given position of the sample \( z \).

Thus

\[
\Delta\phi(z, r, t) = \Delta\phi_o(z, t) \exp\left(-\frac{2r^2}{w^2(z)}\right) \quad (5)
\]

where

\[
\Delta\phi_o(z, t) = \frac{\Delta\phi_o(t)}{1 + \frac{z^2}{z_o^2}} \quad (6)
\]

\( \Delta\phi_o(t) \), the on-axis phase shift at the focus is defined as

\[
\Delta\phi_o(t) = k\Delta n_o(t)L_{eff} \quad (7)
\]

where \( L_{eff} = \frac{(1 - e^{-\alpha L})}{\alpha} \), with \( L \) the sample length and \( \alpha \) the linear absorption coefficient. Here \( \Delta n_o = \gamma I_o(t) \) with \( I_o(t) \) being the on-axis irradiance at focus (i.e., \( z = 0 \)). Ignoring Fresnel’s reflections at the focus \( I_o(t) \) is the irradiance
within the sample. The complex electric field exiting the sample \( E_s \) now contains the nonlinear phase distortion

\[
E_s(r, z, t) = E(z, r, t) e^{-a t / 2} e^{i \Phi(z, r, t)}
\]  

(8)

The resultant electric field pattern is derived after making a Taylor expansion of the phase term in equation (8) and is as follows

\[
E_a(r, t) = E(z, r = 0, t) e^{-a t / 2} \sum_{m=0}^{\infty} \frac{i^m \Delta \phi_o(z, t)]}{m!} \frac{w_m}{w_{m0}} \exp\left(-\frac{r^2}{w^2_m} - \frac{ikr^2}{2R_m} + i\theta_m\right)
\]

(9)

Defining \( d \) as the propagating distance in free space from the sample to the aperture plane and \( g = 1 + \frac{d}{R(z)} \), the parameters in equation (9) are expressed as

\[
w^2_{m0} = \frac{w^2(z)}{2m + 1}
\]

\[
d_m = \frac{kw^2_{m0}}{2}
\]

\[
w^2_m = w^2_{m0} \left[ g^2 + \frac{d^2}{d^2_m} \right]
\]

\[
R_m = d \left[ 1 - \frac{g}{g^2 + \frac{d^2}{d^2_m}} \right]^{-1}
\]

and

\[
\theta_m = \tan^{-1}\left[ \frac{d / d_m}{g} \right]
\]

The transmitted power is obtained by integrating \( E_a(r, t) \) upto the aperture radius \( r_a \) and is expressed as
where $\varepsilon_o$ is the permittivity of the vacuum. Thus including the pulse temporal variation, the normalized Z-scan transmittance is calculated from the equation (1), with $P(I) = \pi w_0^2 I_o(t)/2$, the instantaneous input power (within the sample) and $S = 1 - \exp(-2r_o^2/w_0^2)$ is the aperture linear transmittance, with $w_o$ denoting the beam radius at the aperture in the linear regime.

Fig. 2. Normalized open aperture Z-scan transmittance of Ag nanoclusters in soda-lime glass.
In the present work the experiment was performed with a 8 ns pulse Nd:YAG laser operating at wavelength of 532 nm with an energy density of 11 μJ/cm². The recorded data fitted with the equation (1) is shown in Fig. 2. The value of the nonlinear absorption coefficient of the silver nanocluster composite glass which best fitted with the recorded data is β = ~4.7 m/GW. Thus it can be concluded that the metal nanocluster composite glasses synthesized for the present study are good nonlinear optical materials.