Thermally induced nonlinear refraction of gold and silver polyvinylpyrrolidone nanofluid

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The nonlinear refractive index of metal Au and Ag nano-fluids prepared by γ-radiation method was investigated by a single beam Z-scan technique. Under CW 532 nm laser excitation with power output of 40 mW, the Au and Ag nano-fluids show a large thermal-induced nonlinear refractive index. In the present work it was determined that the nonlinear refractive index for both Ag and Au nano-fluids are -4.80×10^{-8} cm^2/W and -3.85×10^{-8} cm^2/W respectively. The values of Δn_0 for both samples were also calculated to be -2.05×10^{-4} and -1.64×10^{-4} respectively. Our measurements also confirmed that the nonlinear phenomenon was caused by the self-defocusing process making them good candidates for non linear optical devices.

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1. Introduction

The field of nonlinear optics has enlarged a new frontier in science and technology. The major requirements for nonlinear optical materials are; large nonlinear optical (NLO) response, low losses at the wavelength(s) of interest, good optical quality, mechanical stability, easy preparation procedures and low cost. In this context, metallic nanoparticles are known to be among the most suitable and promising materials. Metal nano-fluids has demonstrated a vast range of applications such as, the labeling of biological molecules, surface enhanced Raman scattering, optical limiter and optical photonics devices [1,2]. Z-scan method is one of the simple and accurate methods for measuring the nonlinear optical properties such as nonlinear refraction and nonlinear absorption of solid and liquid samples [3-5]. This method also provides the magnitudes of real and imaginary part of nonlinear susceptibility and the sign of the real part can be simultaneously determined [6-9].

The nonlinear optical properties measurement of metal Au and Ag colloidal solutions prepared using chemical reaction method has been recently reported by Tingjian Jia et al. [10]. Under CW 633 nm excitation they found that all open aperture Z-scan curves were linear. In the present work we report the nonlinear refractive index of Au and Ag nano-fluids prepared using γ (^{60}Co-rays) radiation at 30 kGy level.

2. Experimental details

To prepare Ag nano-fluid sample, 2 mg of silver nitrate ($AgNO_3$ Aldrish-99%), 1.5 g of polyvinylpyrrolidone (PVP, MW 29,000 Aldrish) and 1 ml isopropanol were used. The PVP and isopropanol were used as a colloidal stabilizer and radical scavenger of hydroxyl radical respectively. The PVP solution was made by dissolving PVP powder in 50 ml of deionized water at room temperature. The solution was stirred for 2 hours and was bubbled with nitrogen gas (99.5%) in order to remove oxygen.

The γ-radiation (^{60}Co-rays) source is an effective tool for polymerization process and reducing agent. Silver nitrate ($AgNO_3$) was added into PVP solution and isopropanol, which acted as a hydroxyl radical scavenger. The concentration of Ag nanoparticles in solution was calculated to be 2.35×10^{-4} M. Sample was then irradiated with γ-radiation at a dose of 30 kGy. In this process, γ-irradiation produces hydrated electrons that reduce the silver ions to silver atoms, which then aggregated in the solution. A similar procedure was applied for preparation of Au nano-fluid sample but for this case 2.2 mg of $HAuCl_4.3H_2O$ with 99.999% purity was used. The concentration of Au in solution was 1.295×10^{-4} M. The average diameters of Ag and Au nanoparticles were measured using nanophox machine (Sympatec GmbH, D-38678) and the particles average size were recorded as 26 nm and 10 nm respectively. The linear absorption spectra for both samples were measured using UV-Vis spectrophotometer (Shimadzu-UV1650PC).

Fig. 1 shows the schematic diagram of a single beam Z-scan experiment used in the present measurement. The experiments were performed using a 532 nm laser beam from a diode laser (Coherent Compass SDL-532-150T). The beam was focused to a small spot using a lens and the sample was moved along the z-axis by a motorized translational stage. At the focus point the power output of the laser beam measured was 40 mW. The transmitted light in the far field passed through the aperture and the beam intensity was recorded by a photodiode detector, D. The laser beam waist ω_0 at the focus length was measured to be 24.4 μm and the Rayleigh length was found to satisfy the basic criteria of a Z-scan experiment. A quartz optical cell containing specimen solution was translated across the focal region along the z-axial direction.

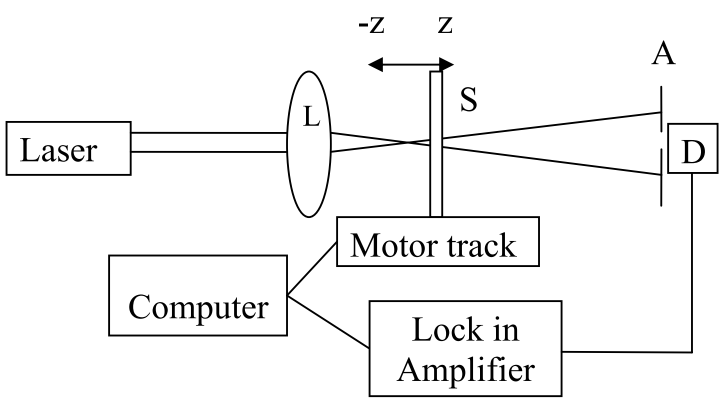

Fig.1. Schematic diagram of a single beam Z-scan experiment setup: L, Lens; S, Sample; A, Aperture; D, Detector.

3. Results and discussion

Figs. 2 and 3 show the absorption spectra for Ag and Au nano-fluids with the surface plasmon absorption peaks located at 410 nm and 532 nm respectively. This gives the thermal induced nonlinearity absorption in Au nano-fluid is greater than in Ag nano-fluid since the surface plasmon peak is the same as the laser used in the present work.

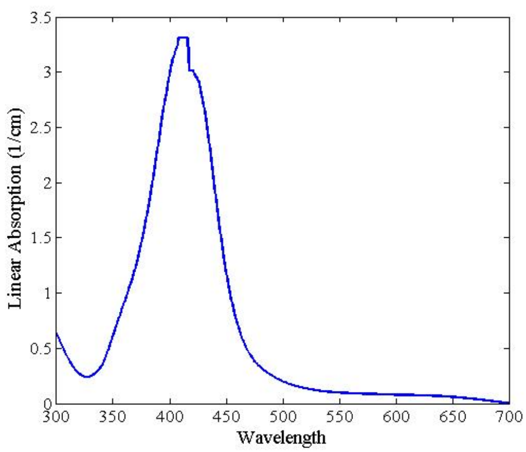

Fig. 2. Absorption spectrum of (Ag-PVP) nano-fluid at concentration of 2.35×10^{-4} M. The average particle size is 26 nm.

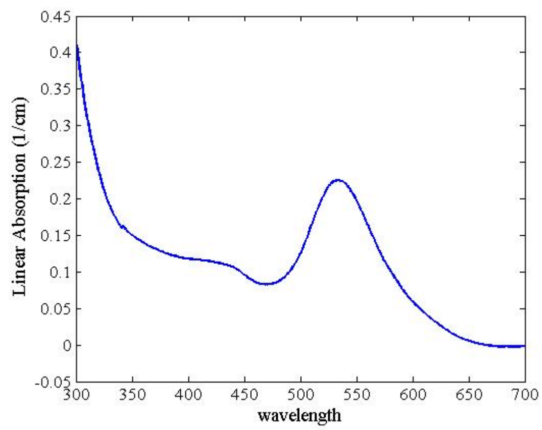

Fig.3. Absorption spectrum of (Au-PVP) nano-fluid at concentration of 1.295×10^{-4} M. The average particle size is 10 nm.

Figs. 4 and 5 show the transmittance curves obtained for Ag and Au nano-fluids. The laser intensity measured was $I_0 = 4.27\times10^3$ W/cm^2 and the aperture linear transmittance was 0.17. The peak-valley curves indicate that the nonlinear refractive index of the medium is negative. Furthermore, the symmetrical shapes show that the two- photon absorption and saturable absorption are very small. Our experimental data were calibrated with data for distilled water in which there is no measurable signals detected.

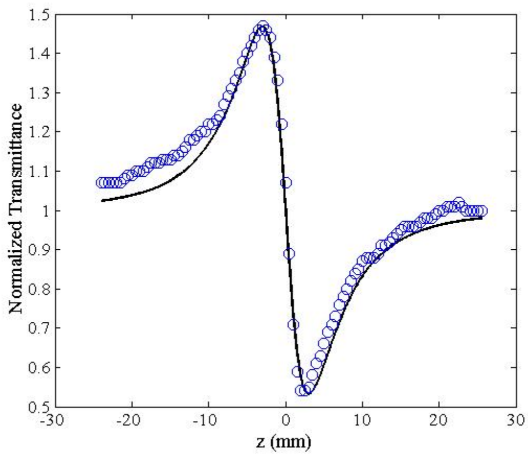

Fig. 4. Closed aperture Z-scan experimental data for (Ag-PVP) nano-fluid under laser excitation at 532 nm wavelength.

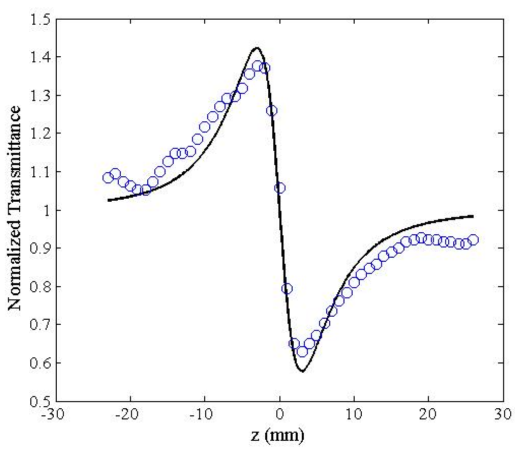

Fig. 5. Closed Aperture Z-scan experimental data for (Au-PVP) nano-fluid under laser excitation at 532 nm wavelength.

The third order nonlinear refractive index, n_2 was calculated using expression reported by Sheik-Bahae et al. [11, 12] as

$$n_2 = \frac{\Delta\phi_o}{kL_{eff} I_o} \tag{1}$$

where $k = 2\pi/\lambda$. I_o is the beam intensity at focus point, and $L_{eff} = \left(1 - \exp(-\alpha L)\right)/\alpha$ is the effective thickness of the sample. In the present work the linear absorption coefficient, α was obtained from the absorption spectra of Figs. 2 and 3. The phase change, $\Delta\phi_o$ was calculated from the experimental data of normalized peak to valley transmittance, ΔT_{p-v} expressed as

$$\Delta T_{p-v} \approx 0.406(1-s)^{0.25}\left|\Delta\phi_o\right| \tag{2}$$

where s is the aperture linear transmittance. The solid line in Figs. 4 and 5 are the calculated values using analytical equation proposed by Liao et al. [13, 14].

$$T(z, \Delta\phi) = 1 - \frac{4\Delta\phi_o x}{\left(x^2+1\right)\left(x^2+9\right)} \tag{3}$$

The shape of curves calculated using Equation (3) are generally in good agreement with the experimental data obtained for both Ag and Au nano-fluid samples. Using the values of I_o and s measured in the present work, we obtained the value of nonlinear refractive index n_2 for Ag and Au nano-fluid sample as -4.80×10^{-8} cm^2/W and -3.85×10^{-8} cm^2/W respectively. Knowing n_2, the change in nonlinear refractive index at the focus can be calculated as $\Delta n_0 = n_2 I_0$ where I_0 being the on-axis irradiance at the focus. This gives the values of Δn_0 for Ag and Au nano-fluids as -2.05×10^{-4} and -1.64×10^{-4} respectively.

Table 1 listed the n_2 and Δn_o for both Ag and Au nano-fluid samples prepared using 30 kGy γ-radiation from ^{60}Co. However in metal nano-fluid we believe that the nano-particle size will give a significant thermal effect to the nonlinearity properties such as nonlinear refractive index and nonlinear absorption. Thus sample preparation technique will be an important aspect in studying nonlinear optical properties of metal nano-particle solution. Since the γ-radiation technique can control the particle size of metal nano-particle in solution, a specific particle size can be produced for specific nonlinear optical devices. This will offer a further nonlinearity study in metal nano-fluids field. The n_2 calculated from Z-scan data can be contributed by electronic (Kerr effect) and thermal mechanisms. However, at lower incident power and nano-particles sample the dominant response is only the thermal effect.

Table.1. The nonlinear refractive index of Au and Ag nano-fluids obtained for Ag and Au samples prepared by γ-radiation method.

Sample	Concentration (M)	Particle size (nm)	n_2 (cm^2/W)	Δn_o	α (cm^{-1})

Ag nanofluid	2.35×10^{-4}	26	-4.80×10^{-8}	-2.05×10^{-4}	0.115
Au nanofluid	1.295×10^{-4}	10	-3.85×10^{-8}	-1.64×10^{-4}	0.225

In this work the lengths of diffraction are larger than those of the samples. So, one can say that the change of radius of the beam caused by diffraction and nonlinear refraction, can be neglected. This assumption simplifies the changes of the intensity and phase of the eclectic field as a function of z' which is governed by a pair of simple equations [11].

$$\frac{d\Delta\phi}{dz'} = \Delta n(I)k \quad (4)$$

$$\frac{dI}{dz'} = -\alpha(I)I \quad (5)$$

where z' is the propagation depth in the sample. Here α(I) is the absorption in which includes the linear and nonlinear absorption terms and k is the wave number of the laser beam. By considering thermally induced nonlinear refraction only, one can express the theoretical description of the thermally induced refractive index change, Δn, as: [15, 16]

$$\Delta n = -(\frac{dn}{dT})\Delta T \approx -(\frac{dn}{dT})\frac{I_0\alpha\tau}{\rho C_p} \quad (6)$$

Here $\frac{1}{\tau} = \frac{1}{t} + \frac{1}{t_c}$, where t is the laser action time, $t_c = \frac{\omega_0^2\rho C_p}{4\kappa}$ is the thermal relaxation time (decay time). The symbols κ, ρ and c_p are presenting thermal conductivity, density and c_p is the specific heat under a constant pressure, respectively. The dn/dT is the change of refractive index with temperature known as thermal-optical coefficient. For a stable system, $\tau = t_c = \frac{\omega_0^2\rho C_p}{4\kappa}$ and by replacing the $\Delta n = n_2^{th} I_0$ in Eq. (6) where n_2^{th} is the effective nonlinear refractive index, we obtain,

$$n_2^{th} = (\frac{dn}{dT})\frac{\alpha\tau}{\rho C_p} = (\frac{dn}{dT})\frac{\omega_0^2\alpha}{4\kappa} \quad (7)$$

The rise time of the thermally induced lens in the liquid is determined by the acoustic transit time, $\tau_r = \omega_0 / v$, where v is the velocity of sound in the liquid. The thermal conductivity of water is 0.6 $Wm^{-1}K^{-1}$, v = 1450 ms^{-1} and with the beam waist $\omega_0 = 24.4$ μm (for 532 nm excitation light), the rise and response times are 17 ns and 1 ms respectively. Hereby, heating caused by a laser beam chopped for a range of frequencies in a few hundred Hz. can be considered as a stable state.

From the Eq. (7) the thermo-optic coefficient dn/dT of Au and Ag nano-fluid can be calculated to be 3.7×10^{-4} and 10×10^{-4} K^{-1}. The magnitude of thermal effective nonlinear refraction coefficient calculated using the thermal parameters are listed in table 2. The values found to be approximately, 1×10^{-8} cm^2/W and in order of our experimental value of n_2. This suggests that the nonlinearity effect in the present samples is thermal induced phenomenon.

Table 2. The thermal parameter for calculation of the effective nonlinear coefficient

	n	C_p	K	dn/dT	ρ
Units		$Jkg^{-1}K^{-1}$	$Wm^{-1}K^{-1}$	K^{-1}	Kgm^{-1}
Water	1.33	4180	0.6	0.95×10^{-4}	1000

In order to verify the our results we carried out measurements of Z-scan with 532 nm laser beam using 2 mm cuvette cell at five different incident powers. Fig. 6 shows the closed aperture Z-scan curves obtained for Au nano-fluid. Fig. 7 shows a linear relationship between the ΔT_{p-v} and the input power P_{in} of the excitation beam. This $\Delta T_{p-v} \propto P_{in}$ agrees with equation (2) where the slope of the line give the nonlinear refraction coefficient, $n_2 = -3.75\times10^{-8}$ cm^2/W close to the experimental value calculated for our Au nano-fluid.

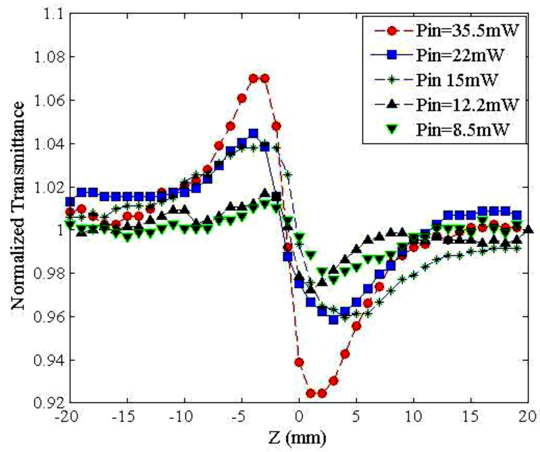

Fig.6. The normalized transmitted of closed aperture Z-scan data for Au nanoparticles measured at five different input powers, 8.5, 12.2, 15, 22, 35.5 mW

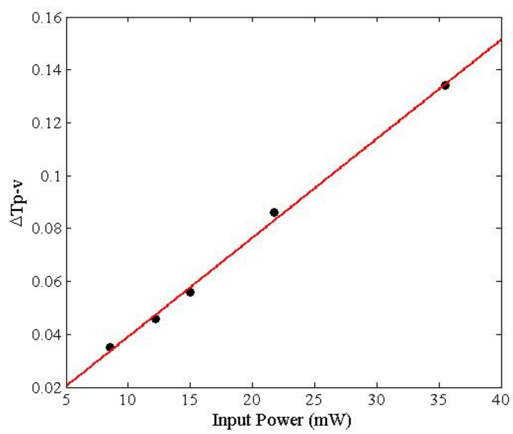

Fig. 7. Relationship between ΔT_{p-v} and P_{in} input power of the excitation beam for Au nano-fluid.

4. Conclusion

Thermal-induced nonlinearity of Au and Ag nano-fluid prepared using γ-radiation method was successfully investigated by a single beam Z-scan technique. The values of nonlinear refractive index, n_2 for Ag and Au nano-fluid obtained using CW 532 nm laser excitation were -4.80×10^{-8} cm^2/W and -3.85×10^{-8} cm^2/W. The values of Δn_0 for both Ag and Au nano-fluids were also calculated to be -2.05×10^{-4} and -1.64×10^{-4} respectively. The experiment also confirmed that the nonlinear phenomenon was caused by the self-defocusing process. This nonlinearity behavior suggests that the present samples could be a good candidate for nonlinear optical device.

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