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Linear and nonlinear optical properties of gold nanoparticles doped borate glasses

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ABSTRACT

Gold nanoparticles (NPs) embedded in sodium antimony borate glass system were fabricated and their optical, physical, structural, ultrafast nonlinear optical properties were studied and analyzed. Metallic gold NPs were synthesized using thermal reducing agent Sb_2O_3 and demonstrated the reduction mechanism of $Au^{3+}/Au^{+} \rightarrow Au^{0}$ by using reduction potentials of corresponding redox system. UV–Visible spectroscopy measurements have revealed the characteristic surface plasmon resonance (SPR) of Au NPs at ~565 nm, attributed due to interband transition. The micrographs of High-Resolution Transmission Electron Microscopy (HR-TEM) confirmed the existence of uniformly distributed spherical shaped Au NPs with particle sizes in the 8–45 nm range with an average particle size of 25 nm. The ultrafast nonlinear optical properties of gold doped glasses were investigated using the *Z*-scan technique at a non-resonant wavelength (λ = 800 nm, 80 MHz repetition rate) with femtosecond (fs) Ti:sapphire laser pulses. Z-scan measurements of undoped glass depicted are verse saturable absorption (RSA) type of nonlinearity whereas the gold-doped glass demonstrated saturable absorption (SA) kind of nonlinearity due to intraband (sp → sp) transitions. The *Z*-scan data demonstrated that the investigated glasses are potential materials for the applications in nonlinear optics devices, particularly in optical switching devices.

1. Introduction

In recent years, the investigations on nonlinear optical (NLO) materials with ultrafast response, high laser induced damage threshold, large two-photon absorption (2PA) and third order nonlinearities have been attempted since these are crucial for the development of next generation photonic devices. Additionally, materials with good optical switching properties are of great interest for waveguide applications [1]. In particular, glasses containing metal nanoparticles (MNP) have drawn significant importance due to their (i) potential applications in; laser physics [1], optoelectronics [2], photovoltaics [3], nanophotonics [4], wavelength converters, super continuum generators, pulse modulators, high speed-high-capacity optical communication system and high-power-short-pulse broad band fiber laser system [5], (ii) high transparency, high mechanical strength, ease of fabrication in desirable shapes and sizes (iii) the MNP concentration dependent NLO response [1] and (iv) use of glasses as a ultrafast optical switchers and limiters since they have fast response time and high Kerr nonlinearity [6]. Further, noble MNP's have fascinated the materials scientists because of their unique properties, including the high scattering and absorption of light resulted from huge optical field enhancements, high electrical conductivity and excellent catalytic property [7–10]. The resonant oscillation of free electrons of the MNPs in the presence of light also known as surface plasmon resonance (SPR) is the origin for enrichment in optical and NLO properties of MNPs [2]. This SPR usually occurs at visible and infrared (IR) regions resulting in effectual resonant light absorption and scattering within a precise spectral range [11]. These properties can be used to exploit light illumination for a variety of applications including photocatalysis, solar cells, sensors, cancer therapy and biological imaging [12–17]. Particularly, gold (Au) NPs are of significant interest due to their capacity to support SPR phenomena and their unique optical properties and it is also due to its low inherent toxicity, an essential requirement for biological applications [18]. For empowering the optical performance of plasmonic nanostructures, it is necessary to tune the peak position, width, and amplitude since by varying the particle size, shape and the composition the SPR or plasmonic properties of NPs can be controlled [11,15,19]. In the absence of intimate contact with a substrate, the peak position of the plasmonic resonance can be tuned by the nanoparticle size [20], shape [21], composition [22] and refractive index of the surrounding dielectric

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medium [23].

The NLO properties of the glasses comprising of MNPs fabricated from different routes were generally investigated at the wavelength that corresponds to the wavelength of the SPRs of these particles [1]. Meanwhile, it is practically important to use the optical switches, optical limiters and other components at the wavelengths of the commercially available lasers, such as Nd:YAG (λ = 1064 nm) and Ti:Al_2O_3 (λ = 800 nm). Therefore, it is essential to study their NLO properties not only in the spectral range of their SPRs, but also at the wavelengths of the commercial lasers towards the development of new materials for practical use in integrated optics and laser systems. The importance of these studies has been understood because the materials possessing strong NLO properties in the near IR range are very attractive for the telecommunication applications. Furthermore, compared to continuous wave (CW) and long-pulsed lasers, the femtosecond (fs) lasers have two distinct features: (i) partial elimination of the thermal effects because of high short energy impeachment time and (ii) high localization of laser photons in both time and spatial domains made possible to assist various nonlinear processes. Because of the ultrafast light–matter interaction time and the high peak powers associated with these pulses, the material processing with fs pulses is generally characterized by an absence of heat diffusion [19]. In literature, there are several reports on the NLO properties of MNPs embedded in silica matrix [5], germanate matrix [24], germano-silicate matrix [25,26], boro-silicate matrix [7], heavy metal oxide matrix [27], phosphate matrix [28], sapphire matrix [29], indium tin oxide matrix [30],TiO_2 matrix [31], and $SrTiO_3$ matrix [32]. However, there are few reports on the NLO properties of borate glasses comprising MNPs. Furthermore, borate glasses possess excellent photonic properties such as good transparency, low glass transition temperature (Tg), high density, high thermal expansion coefficient (allowing easy optical fiber fabrication), optimum bandwidth, good infrared transmission, high mechanical stability, high vitrifying ability and is available at low-cost besides unusual capability to dissolve large amounts of other glass formers, modifiers, rare-earths and MNPs or intermediate compounds without reduction of the glass-forming ability [33]. Particularly, borate glasses containing alkali metals are promising for MNPs formation [33]. These borate glasses consist of intermediate-range ordered micro-domains of boroxol group. Such structural disordering in borate glasses leads to an increase in the average B—O distance in both stable oxygen coordinations of boron (i.e. triangular BO_3 and tetrahedral BO_4) [34]. It was recently demonstrated by Youngman et al. [35,36] that near the glass-transition temperature the boroxol rings breakup leads to more open structure in borate glasses. Therefore, alkali borate glasses are an interesting host material for experiments with metallic MNPs formation. The present work reports on optical, structural and ultrafast non-resonant (fs laser operating at wavelength, λ = 800 nm was used) NLO properties of gold doped Sb_2O_3—Na_2O—B_2O_3 glasses.

2. Experimental details

2.1. Samples preparation

The glasses of nominal composition $2Sb_2O_3$–$25Na_2O$–$73B_2O_3$–$xAuCl_3$ (x = 0, 0.005, 0.01, 0.02 mol%, hereafter named as NB–0, NB–1, NB–2, NB–3 respectively) were prepared by melt quench technique. The proper weights of AR grade Sb_2O_3, Na_2CO_3, H_3BO_3, and $AuCl_3{\cdot}HCl{\cdot}xH_2O$ chemicals were mixed homogenously and the composition was taken in a porcelain crucible and kept in high temperature furnace. Initially, the batches were maintained at about 450–500 °C for 30 min for complete decarbonisation of Na_2CO_3 and the decomposition of H_3BO_3 and the temperature was raised and maintained at 1160^0C of about 50 min. The crucibles were shaken frequently at interval of 15 min for a uniform mixing of all the glass constituents. The glass melts were quickly cooled at room temperature by pouring and pressing between two pre-heated brass moulds after the complete melting. The as prepared glasses were ruby in colour and the glasses were polished for further characterization with post annealing of the samples at 350 °C for ~4 h to remove the thermal stresses in glasses. A good reproducibility was achieved in gold doped glasses. The circular disc shaped glass samples with typical thickness of ~1 mm (in particular, the thickness of the NB–0, NB–1, NB–2 and NB–3 glasses were 0.98 mm, 0.95 mm, 0.97 mm and 0.99 mm, respectively) were used for characterization.

2.2. Characterization of the glasses

XRD (Rigaku Ultima IV) measurements using Cu-Kα radiations (λ = 1.54 Å) with copper filters operating at 40 kV and 100 mA, the range of 2θ was 0^0–60^0 with step size of 0.2^0, a resolution of 0.01^0were used to confirm the glassy nature of the samples. The room temperature optical absorption spectra were recorded using PerkinElmer Lambda–35 UV–Vis spectrometer in the range of 200–1100 nm equipped with a deuterium lamp and halogen lamp with a resolution of ± 1 nm. The refractive indices measurements were made using Abbe's refractometer having mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer, and sodium vapour lamp emitting the light of wavelength of 5893 Å (D line) was used as a source of light, the measurements of refractive indices were repeated for consistency and all obtained values were similar with an error of ± 0.0001. Technica G2, F30 High- Resolution Transmission Electron Microscope (HR-TEM) operating at accelerating potential of 300 kV with resolution of 2 Å was used to obtain the structural morphology, size distribution and to verify the existence of gold NPs in the glass matrix. Fourier transform infrared (FTIR) transmission spectra of all glass samples were taken by a Thermo Nicolet, Avatar 370 FTIR spectrometer in the range of 400–4000 cm^{-1} with resolution of 4 cm^{-1} using KBr pellet technique. The ultrafast nonlinear optical measurements were made using *Z*-scan technique [37]. In Z-scan experiments, fs pulses from a Ti:sapphire laser (Chameleon, Coherent Inc., 80 MHz, ~150 fs) were utilized. The wavelength of 800 nm (non-resonant wavelength) was selected in the present experiments. In the far field, a perfect Gaussian profile of the input bean was obtained by spatial filtering. In *Z*-scan measurement, the input beam of 2–mm diameter was focused using 10 cm focal length convex lens and the glass sample was placed on a 10-μm resolution translation stage. The data was collected manually using a detector (Thermal Sensor-Field Max, Coherent). Since the Z-scan technique is a sensitive technique, to avoid the errors in the collected data, the samples having high polish, uniform thickness were used for measurements and the measurements were repeated with the same intensity. The obtained NLO coefficients were within the experimental estimated error of ± 10% for both open aperture and closed aperture data. The main sources of errors in such measurements are from the peak intensity estimation, laser pulse to pulse fluctuations, and fitting errors.

3. Results and discussion

3.1. X-ray diffraction and UV–Vis absorption spectroscopy

The absence of sharp crystallization peak and presence of a broad hump at 40^0–55^0 confirms the glassy nature of the samples. Fig. 1 presents the typical XRD patterns of all the samples and are nearly same. The concentration of gold in present glasses is very low and, therefore, no characteristic peak of Au was evident in the spectra [38]. The absorption spectra of glasses containing MNPs are always very much responsive to the size, shape and interparticle distance and dielectric function of the MNPs [38,39]. The optical absorption spectra for glasses doped with different concentration of gold displayed in Fig. 2 (a), in which inset showing the absorption spectrum of undoped (NB–0) glass. The undoped glass did not demonstrate any absorption band. However, the clear proof of SPR absorption band near 565–597 nm (due to the interband transition from the 'd' band to the