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Optical, structural and Near-IR NLO properties of gold nanoparticles doped sodium zinc borate glasses

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ABSTRACT

Gold (Au) nanoparticles (NP) embedded borate glasses with the molar composition of (x-0.1) $Na_2O-10ZnO-(90-x)B_2O_3-0.1AuCl_3$ (x = 10, 20, 30 mol %) have been prepared via melt quench technique. The effect of Na2O content on properties such as optical, structural and nonlinear optical (NLO) properties of gold NPs containing sodium zinc borate glasses were studied using UV-Visible absorption, Fourier Transform Infrared spectroscopy (FTIR), High Resolution-Transmission Electron Microscope (HR-TEM) and Z-scan measurements. X-ray diffraction (XRD) measurements confirmed the glassy nature of the samples. UV-Visible absorption spectra of glasses comprising Au NPs demonstrated a broad surface plasmon resonance (SPR) absorption peak near 577 nm due to the transition from d-band to the Fermi level and this SPR peak demonstrated a red-shift with increase in Na₂O concentration. HR-TEM micrographs revealed the presence of uniformly distributed and spherical shaped Au nanoparticles with an estimated average particle size of $\sim 6 \text{ nm}$ ($\pm 1.5 \text{ nm}$). Nonlinear Optical (NLO) measurements were performed at three different off-resonant wavelengths (750 nm, 800 nm, 850 nm) using femtosecond (fs) pulses (150 fs, 80 MHz) delivered by aTi:sapphire oscillator. Saturable Absorption (SA) kind of nonlinearity has been observed in the open aperture (OA) Z-scan data and is attributed to intraband transition within the Au NPs, while the closed aperture (CA) Z-scan data illustrated a negative type of nonlinear refraction attributed to effect of self-defocusing. NLO studies and the obtained nonlinear coefficients suggest that, the NZB glasses are potential candidates for mode-locking and switching applications in nearinfrared spectral region.

1. Introduction

In recent decades, noble Metal Nanoparticles (MNPs, e.g. Cu, Ag, Au) have drawn special attention due to their notable optical properties owing to the resonance oscillation of the free electrons also known as Surface Plasmon Resonance (SPR) [1]. In the recent past, the optical and nonlinear optical (NLO) properties of MNPs have been studied extensively since these nano-sized particles find applications in different fields like photonics, bio-imaging, solar energy conversion, optical data storage, sensors. Further, the MNPs can also be used as catalysts because of their large surface-to-volume ratio [2,3]. When the suitable wavelength of light strikes a metallic nanoparticle (NPs) SPR occurs, which results in the collective oscillation of plasma of conduction electrons. Furthermore, when intense laser radiation interacts with

NPs it results in the excitation of a variety of nonlinear processes. Glasses which host with MNPs are promising materials for the development of optical devices (particularly NLO devices) associated to their large NLO coefficients, intensified absorption frequencies with ultrafast response times due to the SPR of MNPs [4]. The most common method for preparing the glass-metal nanocomposites is by introducing metal ions viz., ion implantation, ion irradiation and ion exchange etc. in synthesized glasses or in commercial available glasses followed by long heat treatment or laser irradiation (both promoting NPs precipitation within the glass host) to achieve NPs by metal reduction [5,6]. A controlled synthesis of metal-glass nanocomposites with well-defined and highly stable NPs is desirable for the above mentioned potential applications. The optical properties of MNPs in glasses are strongly influenced by their size, shape and dielectric constant of surrounding

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medium. Often, narrow size dispersion is a necessary condition for practical utilization of the MNPs. Among several techniques for fabricating metal-glass nanocomposites, the melt quench technique is the most reliable to embed the metal NPs homogenously in the glass matrices when the concentration of metal NPs is low. These glass-nanocomposites can be used as biosensors, as a photocatalysts, as optical limiters in photonic devices and also as distinct agents in nonlinear microscopy [7]. The investigation of nonlinear refraction and absorption at optimum operational wavelength (i.e. at infrared region) is essential for developing the materials for practical photonic applications. It has been recently understood and reported that, compared to long laser pulses, femtosecond (fs) pulses have advantages such as (a) reduction of the thermal effects since energy deposition time is too small and (b) the localization of photons in both time and the spatial domains is high resulting in various localized nonlinear processes, enabling higher resolution in imaging [8]. There are numerous reports on the NLO properties of MNPs incorporated in diverse glasses [8-12]. The phosphate glasses possess good solubility of other glasses formers, glass modifiers, rare earths (REs) and MNPs. Silicate and germanate glasses also possess strong nonlinearity. However, the poor stability against the moisture attack (particularly of phosphate glasses) combined with high glass transition and melting temperatures of silicate and germanate glasses limits the practical applications of these glasses. Therefore, it is of important to explore new glasses with high optical nonlinearity and desirable optical properties. In view of this, borate glasses are the alternatives since these glasses possess excellent photonic properties like good transparency, low glass transition temperature (Tg), optimum bandwidth, good infrared transmission, easy optical fibre fabrication due to high thermal expansion coefficient, excellent mechanical stability, superior vitrifying ability and also they are available at low-cost with amazing capacity to dissolve large amounts of other glass formers, modifiers, rare-earths (REs) and MNPs or intermediates without reducing the glass forming ability [13]. Further, the alkali borate glasses are promising for MNPs production [13] and, in particular, the sodium zinc borate glasses have already been studied extensively for their conducting and luminescence applications and also this glass matrix is very stable against thermal and moisture attack. Furthermore, the NLO properties of these metal NPs doped glasses and the origin of the optical nonlinearity have not been studied indetail in any of the previous reports. The present work involves the systematic study of influence of additive concentration of Na2O on optical, structural and NLO properties (NLO measurements were studied at significant wavelength region of 750-850 nm since this is the output wavelength region of commercially available fs lasers and these fs lasers are common sources by researchers towards biological applications) used of Na₂O-ZnO-B₂O₃ glasses containing gold NPs.

2. Experimental details

2.1. Preparation of glass samples

A series of sodium zinc borate glasses with wide molar concentration of $(x-0.1)Na_2O-10ZnO-(90-x)B_2O_3-0.1AuCl_3$ (x = 10, 20, 30 mol %) have been fabricated through the most common melt quench method, here after the samples are coded as 1NZB, 2NZB, 3NZB for the glasses which contain 10, 20 and 30 mol% of Na₂O, respectively. Analytical Reagent (AR) grades of sodium carbonate (Na₂CO₃), zinc oxide (ZnO), boric acid (H₃BO₃), and chloroauric acid (AuCl₃·HCl.xH₂O) were used as starting materials for preparation of glass samples. All the chemicals were well mixed in mortar, grinded well with pestle then the fine powder was transferred in to porcelain crucibles. The crucibles were kept in high temperature furnace for melting. The batches were maintained at 550 °C for about 20 min initially for complete de-carbonization of sodium carbonate and then the temperature was slowly raised to 1000 °C and maintained at around 10 min for decomposition of boric acid. Finally, the melted batches were maintained at 1050 °C at about 30 min with constant stirring at an interval of 15 min and then glass samples were obtained with sudden quenching of melts on pre–heated (at 200 °C) brass molds. The finely polished (polishing was performed using commercially available emery papers) circularly shaped glass samples having diameter of ~10 mm and thickness of ~1 mm were used for further characterization with post annealing (at 300 °C) to remove any thermal stresses in the glasses which possibly could have been produced during the quenching.

2.2. Characterization of the glass samples

To confirm the lack of crystallinity in the prepared glass samples. X-ray diffraction (XRD, Rigaku Ultima-IV operating at 40 kV and 30 mA, Cu K- α radiation of wavelength $\lambda = 0.15418$ nm) measurements were done in the diffraction angle (2 θ) range between $0^{\circ} - 60^{\circ}$ with step size of 0.02°. Portable Abbe's refractometer (with source of light being sodium vapor lamp, D-line, $\lambda = 5893$ Å) was used for refractive index (n) measurements in which the contact layer between the sample and prism of the refractometer is monobromonaphthalene. The values of refractive indices (of the samples under study) were within the allowed range of \pm 0.001 around the mean value after repeating the experiment several times for sake of consistency in the results. Using Perkin Elmer lambda-35 UV-Visible spectrometer (having the resolution of \pm 10 Å) the linear absorption data of polished bulk glass samples was collected at room temperature (RT) in the spectral range of 200-1100 nm. Finely powdered glass samples were used for the thermal investigations in the temperature range of 50 °C – 400 °C with heating rate of 10 °C/min in nitrogen atmosphere using Mettler Toledo Differential Scanning Calorimeter (DSC) star system. The structural studies of all the glass samples have been done using a Fourier Transform Infrared (FTIR) spectrometer in the wave number limits of 400–4000 cm^{-1} range possessing a resolution of 4 cm^{-1} using KBr pellet technique. To confirm the existence and to know the distribution of Au NPs in glasses, High Resolution-Transmission Electron Microscope (HR-TEM, operating at an accelerating potential of 300 kV with a resolution of 2 Å) measurements were done. The average particle size, shape and morphological studies of the NPs have been done using ImageJ software and the average particles size calculations were repeated to minimize the error. It is found that the particle size values are nearly identical within an error of ± 1.5 nm. The NLO properties were realized using conventional Z-scan technique [14], in which femtosecond (fs, ~ 150 fs) pulses delivered at a repetition rate of 80 MHz were utilized from a tunable (680 nm-1060 nm) Ti: sapphire laser (Chameleon, M/s Coherent). The NLO measurements were carried out at three non-resonant wavelengths ($\lambda = 750$ nm, 800 nm, 850 nm). In Z-scan experiments the glass sample was moved slowly along the scan axis (Z-axis, i.e. from -Z to + Z) of the laser beam using a translation stage. The transmission of the laser light changed for every corresponding Z-position and this change of transmission of laser light was monitored by using an energy meter. The reproducibility of the obtained results has been confirmed by repeating the experiments multiple times. The intensity of the transmitted laser beam from the bulk glass varies based on the position of the sample and will be maximum or minimum at the focus based on the material nonlinear absorption property. For all the glass samples and at all three different excitations, similar peak intensities were maintained. Details of the complete Z-scan experimental procedure can be found in our earlier work [9].

3. Results and discussion

3.1. XRD studies

To disclose the amorphous nature of the prepared glasses, XRD measurements were executed on powder glass samples. The XRD profiles of all the prepared glasses represented in Fig. 1 and in all the cases the patterns are nearly same. The wider peak or broad hump centered at



Fig. 1. XRD profiles of NZB glasses studied in this work.

 45° ($\pm 2^{\circ}$) of 20 with no sharp in Fig. 1 strongly, confirming the glassy or non-crystalline feature of the prepared samples. The peaks due to gold NPs in NZB glasses did not appear since the concentration of gold was very low and the similar observations were reported in some of the earlier works [15,16].

3.2. Optical properties

The prepared glass hosts with gold NPs were ruby in color and to know the reason substantially for the appearance of color, the optical absorption measurements were performed. The absorption spectra of Na₂O–ZnO–B₂O₃ glasses containing Au NPs with varied concentration of Na₂O were taken at RT (i.e. at 300 K) and are illustrated in Fig. 2. In absorption spectra the SPR band of Au NPs is observed with a larger shoulder near 577 nm (2.14 eV) and this SPR peak is due to the transition from d–band to Fermi level within Au NPs [17] and it also known as interband transition, whereas the glasses which are free from gold NPs (transparent) did not demonstrate any absorption peak (data not shown here) which suggests that the appearance of ruby color can possibly be attributed to that SPR band. The amplitude (height) of SPR peak of the gold MNPs increases with increase in Na₂O concentration.



Fig. 2. The absorption spectra of NZB glasses with different concentration of Na_2O , the dotted vertical representing red–shift of the SPR peak of Au NPs with respect to concentration of Na_2O . (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Optical and thermal properties of NZB glasses at different concentration of Na_2O .

Glasses and Properties	1NZB	2NZB	3NZB
Optical Properties			
Refractive index, n (\pm 0.001)	1.654	1.662	1.674
Position of SPR peak (± 1 nm)	577	586	592
Direct energy bnadgap E_g^{dir} (eV, $\pm 0.005 \text{ eV}$)	3.734	3.581	3.421
Indirect bandgap energy, E_g^{indir} (eV, $\pm 0.005 \text{ eV}$)	2.667	2.378	2.056
Urbach energy ΔE , (eV, $\pm 0.002 \text{ eV}$)	0.868	1.007	1.173
Thermal Properties			
Glass transition temperature (Tg, \pm 1 0 °C)	292	319	342

This enhancement in amplitude of SPR peak of Au NPs indicates that the size of the Au NPs grew as Na₂O concentration increased [18]. From the literature it is clear that, the position of SPR peak of MNPs is highly sensitive to the variation in the dielectric constant and/or refractive index, the concentration, the size and shape of the MNPs [19]. As the data illustrated in Fig. 2, the SPR band of gold NPs was found to shift towards the longer wavelengths (represented by dotted vertical line in Fig. 2) from 577 nm to 592 nm (± 1 nm) when concentration of Na₂O raised from 10 mol% to 30 mol% (in particular, the SPR peaks of Au NPs in 1NZB, 2NZB, 3NZB were observed at 577 nm, 586 nm and at 592 nm, respectively). The similar trend (i.e. shift of SPR peak of Au NPs towards longer wavelength side) of SPR peak shift was also observed by Ghoshal et al. and Amjad et al. for gold and silver NPs, respectively [16,19]. In former case they realized the red-shift of SPR peak of Au NPs with increase in Au concentration, in the latter case they observed red-shift of SPR peak of silver NPs with respect to heat treatment at above glass transition temperature and also in later case the shape of the silver NPs was not spherical. The uncertainty of the SPR band position is ± 1 nm. From the data presented in Table 1, it is evident that an increase in the refractive index of the glasses was observed with increase in mol% of sodium. It has been reported that, the addition of alkali or alkaline earth metal oxide (here Na₂O) in to the glass network leads to the formation of several BO₄ structural groups and hence increases the number of non-bridging oxygen (NBOs) content at the expense of bridging oxygens (BOs) [20]. Since the NBOs are more polarizable than BOs [21] and also there is a direct inter--relationship between polarization and refractive index, therefore the refractive index increases with increase in Na₂O. From these arguments it can be concluded that the SPR of peak of the Au NPs is red-shifted with increase in refractive index. A similar observation (i.e. SPR peak of MNPs shift towards as increase in refractive index) has been made by Ghoshal et al. for Au NPs in tellurite glass matrix [16] and Ju et al. for Au NPs in silicate matrix and in germano-silicate matrix [22,23]. This red-shift of SPR peak can be explained as follows: at higher wavelength of the incident light, due to the increase of the wave vector of the surface plasmon mode, resonance condition is achieved and results in the SPR peak of MNPs shift towards longer wavelengths of MNPs (here Au) with the enhancement in the refractive index [22]. It has been demonstrated that, the change in the oxygen bond strength in the glass structure affects the absorption characteristics of the glasses and in turn affects the absorption edge in the glasses [24].

The linear absorption coefficients α (λ) of the prepared glass samples was estimated using the relation,

$$\alpha(\lambda) = 2.303 \left(\frac{A}{t}\right) \tag{1}$$

where, 'A' and 't' are the absorbance and the thickness of the bulk glass samples respectively. Based on the hypothesis of electronic structure of the glasses, the optical absorption edge in glasses can be evaluated and it is vital in order to understand the network of the glass and also for understanding their optically induced transitions that can be done using absorption data of the glasses. At the fundamental absorption edge of amorphous and crystalline materials the two types of optical transitions (the direct and indirect) can occur. When the electromagnetic waves interact with the electrons which are present in valence band and are raised to the conduction band through the fundamental optical band gap, gives rise to both the direct and indirect transitions [25]. Using the Davis and Motto theory, the energy of optical band gap in the vitreous materials can be evaluated through direct and indirect allowed transitions [26]. According to Davis and Motto [26], the ' α ' and the ' $h\nu$ ' related as,

$$\alpha h\nu = B'(h\nu - E_{opt})^m \tag{2}$$

where, ' α ' is the linear absorption coefficient, ' $h\nu$ ' is the photon energy of incident radiation, B' is constant (known as band tailing parameter), E_{opt} is the optical band gap energy, 'm' is the index number through which the kind of transition causing the absorption can be decided. Typically, the 'm' takes the values as 2, 1/2, 3 and 1/3 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions respectively and also the value of 'm' depends on the type of material (crystal or amorphous). In non-crystalline materials the absorption edge E_{opt} has a finite slope, whereas in crystalline solids there is sharp well-defined lattice absorption edge E_{opt}. Thus, according to Tauc's relation, m = 2 is desirable since indirect transitions are valid in amorphous materials [27]. The linear regions of $(\alpha h\nu)^2$ v/s h ν and $(\alpha h\nu)^{1/2}$ v/s h ν were extrapolated to meet h ν at $(\alpha h\nu)^2 = 0$ and $(\alpha h\nu)^{1/2}$ $^{2} = 0$ to evaluate the values of direct (E_{g}^{dir}) and indirect (E_{g}^{indir}) bandgap energies. The dependence of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ on $h\nu$ related to the direct and indirect allowed transition of the prepared sodium zinc borate glasses are depicted in Fig. 3(a) and (b) respectively. When the Na₂O concentration is increased from 10 mol% to 30 mol% in present glasses the E_g^{dir} values decreased from 3.734 eV to 3.421 eV and E_g^{indir} decreased from 2.667 eV to 2.056 eV. The variation of E_g^{dir} and E_g^{indir} values is shown in insets of Fig. 3(a) and (b) respectively and are tabulated in Table 1 with an estimated error of ± 0.005 eV. The range of indirect optical bandgap energies (2.667-2.056 eV) of present glasses are higher than the values reported in rare earth (RE) doped borate (1.70-1.36 eV) [28,29] and phosphate glasses (1.78-1.66 eV) [29] while closer to antimony-borosilicate (2.65-2.52 eV) [29] and lesser than germinate–borate glasses (5.5–4.1 eV) [29]. This decrease in $E_{g}^{\ dir}$ and E_g^{indir} values attributed to the increase in NBOs number with raise in Na₂O mol% leading to the shifting of the band edge to lower energies side [30]. Urbach [31] assumed that, near the absorption band edge the absorption coefficient ' α ' exhibit an exponential behaviour with respect to photon energy 'h ν ' and empirically the equation being followed is as below,

$$\alpha(\nu) = \alpha_0 exp\left(\frac{h\nu}{\Delta E}\right) \tag{3}$$

where, ' α_0 ' be the constant and ' ΔE ' is the Urbach energy. Relation relating valence and conduction bands with band tails which extend in to the band gap, leads to the exponential behaviour of optical bandgap.

The strength of disorder in the glassy materials can be explained using the values of the Urbach energy (ΔE), the width of localized states in bandgap. Materials with greater impulse to convert weak bonds into defects exhibit larger value of Urbach energy (ΔE). The calculation of ΔE values were done from the reciprocals of the slopes of the plots of ln (α) v/s h ν and the dependency of ln (α) on h ν is shown in Fig. 3(c). From inset of Fig. 3(c) and also from the Table 1, it is clear that, the ΔE is increasing with increase in Na₂O mol% in the investigated glasses. This clearly indicates that the substitution of Na₂O in to the glasses increases the disorder of glass systems. In Table 1, the error of enlisted Urbach energy values is \pm 0.002 eV.

3.3. Structural properties

FTIR spectroscopy is the best characterization method to understand the structural bonding, fundamental and functional groups in



Fig. 3. (a) Plots of $(\alpha h\nu)^2 v/s h\nu$ for direct energy band gap measuremerements, (b) plots $(\alpha h\nu)^{1/2} v/s h\nu$ for indirect energy band gap measurements, (c) plots of ln (α) v/s h ν for Urbach energy calculations. Insets of Fig. 3(a), (b) and (c) represents the variation of direct energy band gap, indirect energy band gap and Urbach energy with respect to Na₂O concentration, respectively.

crystalline and amorphous materials [32]. The FTIR spectra of the sodium zinc borate glasses with different concentration of Na₂O were recorded from 4000 cm⁻¹ to 400 cm⁻¹ and are depicted in Fig. 4. The FTIR spectra provide the information regarding various bonding between different ions in the glass network. The transmission band positions (within ± 4 cm⁻¹) and assignments of examined glasses are



Fig. 4. FTIR spectra of the NZB glasses studied in this work.

summarized in Table 2. In the FTIR spectra broad bands have been observed, which are attributed to the amalgamation of vibrational states of higher degeneracy, lattice dispersion thermal broadening and mechanical scattering of the powdered samples [9]. From the data presented in Fig. 4, it is apparent that there is no detectable variation in the peak position as increase in the sodium concentration. Generally, the borate glass network consists of three important regions of vibrational modes: (i) the bands occur between 1220 and 1600 cm^{-1} are due to the asymmetric stretching vibration of B–O bonds belonging to BO₃ units, (ii) the bands located in the range of $800-1200 \text{ cm}^{-1}$ are due to the B–O bond stretching contributing from of the tetrahedral BO₄ units and (iii) the vibrational bands are lies in the region around 700 cm^{-1} are due to the bending of B–O–B linkages in the borate network [33]. In Fig. 4, the band at 1618 cm^{-1} is attributed to O–H bending vibration due to absorption of moisture by the sample from the environment, the absorption band appearing near 1396 cm⁻¹ is attributed to the stretching relaxation of the B-O bond of the trigonal BO₃ units, the absorption band located around 1052 cm⁻¹ is due to stretching of B-O bonds in tetrahedral BO₄ units of borate network [34], a weak absorption band at around 855 cm⁻¹ is identified due to the stretching vibrations of B–O bonds in BO₄ units from diborate groups [33]. The band at 710 cm⁻¹ is attributed to the bending vibrations of B-O-B linkages in the borate network [35]. The presence of vibrations of ZnO₄ structural units cannot be ruled out in present sodium zinc borate glasses as there is a presence of some weaker bands in IR spectrum of these glasses around 460 cm⁻¹ [34]. Generally, the IR absorption band at 806 cm⁻¹ is attributed to the boroxol ring in the borate glass network [36]. In the present investigation, the band at 806 cm^{-1} is absent, which reveals the absence of boroxol ring in the glass network.

The existence, shape, size and distribution of Au NPs have been identified using HR–TEM images. The HR-TEM micrographs of 3NZB glass are shown in Fig. 5. Fig. 5(a) confirms the existence of Au NPs while Fig. 5(b) represents uniform distribution of the Au NPs in glass with almost spherical shape. Fig. 5(c) illustrates the size distribution

(histogram) of the Au NPs in 3NZB glass, from which it is evident that the glass contains gold NPs with an average particle size of ~6 nm (\pm 1.5 nm) with wide size distribution ranging from 2 nm to 12 nm. The selected area of electron diffraction (SAED) pattern of Au NPs is shown in Fig. 5(d). The spherical rings around the central bright region also confirm the existence of Au NPs in the glass matrix and planes in Au NPs were assigned according to JCPDS card no. 4–784. Further, Smithies et al. [37] demonstrated that, the sodium acts as an alternative reducing agent and which forms stable MNPs of smaller size, and also in Fig. 3, the IR spectrum of gold free 3NZB glass (i.e.30Na₂O–10ZnO–60B₂O₃) is similar that of gold containing 3NZB glass (i.e.29.9Na₂O–10ZnO–60 B₂O₃–0.1AuCl₃) means that, no additional bands are observed in the spectrum. It concludes that, the gold is not forming any linkage with glass network and gold situated as NP in the present glasses.

3.4. Thermal properties

The thermal properties of the prepared glasses were investigated using DSC measurements to determine the effect of glass composition on glass stability. Fig. 6 represents the representative DSC profile of 1NZB glass. The heat flow values are directly obtained from the DSC related software available with the equipment during the measurement. Glass transition temperature (T_g) is a significant feature, which is exhibited by the super-cooled liquids and play important role in material properties. The extrapolated temperature Tg for onset of rapid rise of the Heat flow v/s Temperature plot is determined using the width of the glass transition region as measured during heating by DSC. From Table 1, it is evident that, Tg increases with increase of Na₂O concentration. This increase in T_g with respect to Na₂O mol% indicates the enhancement in the strength and connectivity of the glass structure [25]. This increase in T_{g} suggests that, the thermal stability of 30 mol % of Na₂O is the highest. The highest Tg value of 3NZB glass demonstrate the best thermal stability and least tendency of devitrification. The large (T_g 342 °C, refer Table 1) value for the present borate glass (3NZB) is much larger than that of tellurite TZNE glasses (i.e. 70TeO_2 -20ZnO-10Na₂O-(x)Er₂O₃-(y)Au (x = 0.0 and 1.0 mol%; y = 0.0, 0.2, 0.4 and 0.6 mol%, Tg = 224 °C). The TZNE glass is known as a promising host for fiber devices due to its good thermal stability [16]. The large T_g values of 3NZB glass demonstrate that, the 3NZB glass is the better choice for glass performance and fiber drawing applications.

3.5. NLO properties

A number of new NLO studies have been reported recently due to rapid development in the fields of nanoscience and nanotechnology. The design and fabrication of nanoscale optoelectronic and photonic devices has been promoted because of remarkable NLO properties possessed due to continuous growing of number of nanomaterials. The fields like laser technology, communication, information and image processing, optical computing and data storage are widely using nonlinear optics, hence it has a great value and far-reaching scientific significance. Since the Au NPs play a very prominent role in the field of

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FTIR	band	positions	and	assignments	of NZB	glasses
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Glass Samples and Wave numbers in cm $^{-1}$ (\pm 4 cm $^{-1})$		$\pm 4 \mathrm{cm}^{-1}$)	Band Assignments
1NZB	2NZB	3NZB	
1618 1396 1052 855 710	1620 1396 1056 857 713	1622 1398 1059 861 717	O–H bending vibration due to absorption of moisture by the sample from the environment stretching relaxation of the B–O bond of the trigonal BO_3 units stretching of B–O bonds in tetrahedral BO_4 units of borate network the stretching vibrations of B–O bonds in BO ₄ units from diborate groups bending vibrations of B–O b linkages in the borate network



Fig. 5. HR–TEM micrographs. (a) Indicates the presence of Au NPs (b) illustrates that the Au NPs are spherical in shape and distributed uniformly (c) Histogram of the Au NPs to estimate the average particle size of the Au NPs (d) SAED pattern of the Au NPs.



Fig. 6. Typical DSC profile of 1NZB glass.

photonics [38], characterizing the NLO properties in the near IR region is important for device applications since most of the commercially available lasers are operating in this region. Therefore, NLO measurements were carried out at extended spectral range of 750 nm-800 nm in steps of 50 nm using Z-scan technique. In Z-scan experiment, the bulk glass samples were exposed to laser light in the far field, i.e., $|Z| \gg 0$, in the far field the beam radius is large thus the photon flux is small. Therefore, in the far field the light transmission is independent of Z, i.e. transmission is constant, because only single-photon absorption is responsible for light absorption. Whereas, at focus the photon flux is high, and nonlinear processes are possible. Typically, nonlinear processes are distinguished in a Z-scan experiment based on decrease in transmission at Z = 0, revealing RSA like behavior while increase in transmission at the focal point, revealing SA behavior. In Z-scan, open-aperture (OA) and closed-aperture (CA) Z-scan techniques have been employed for the measurement of the absorption and refraction (nonlinear) of the

bulk samples respectively. In the present investigation, for consistency sake the measurements were repeated several times and estimated values are within an error of \pm 10% in both OA and CA Z-scan data. The errors in these measurements arise mainly from the uncertainty in estimating the spot size at focus apart from input laser fluctuations and data fitting errors. Usually, different possible mechanisms occur in metal nano-clusters viz., the interband and intraband transitions, multi-photon absorption and induced thermal scattering. One or more of these effects can be caused by laser pulses based on the absorption of energy by the NPs, medium of the surrounding and the wavelength of excitation [39]. Fig. 7(a-c) show the non-linear absorption (OA Z-scan signatures) of sodium zinc borate glasses host with Au NPs at excitation of 750 nm, 800 nm, 850 nm, respectively, in which the open circles represent the experimental data whereas the solid lines represent the theoretical fits. At the excitation wavelengths, the linear transmittance of \sim 74% (nearly) has been observed for all the glass samples and all the measurements were done at input peak intensity of about 8.2×10^8 Wcm⁻². The incident laser irradiance is low and transmittance is almost constant when the sample is away from the focus, but around the focal point the absorption coefficient is affected by the optical nonlinearity resulting a peak at Z = 0 in the present investigation corresponding to an increase of the transmittance, i.e., saturable absorption (SA) nonlinearity. The measured nonlinear transmission curves were used to evaluate and to discuss the contributions of SA like nonlinearity. Within the sample the irradiance 'I' varies due to the optical absorption of the sample and which follows the equation given by

$$\frac{dI}{dz} = -\alpha(I)I \tag{4}$$

where 'z' is being distance of propagation within the sample and ' $\alpha(I)$ ' is the absorption coefficient dependent with irradiance. When there is no nonlinearity in the sample [i.e. $\alpha(I) = \alpha_0$] then the equation (4) is simplified in to Beer–Lamberts law of optical absorption [40,41]. For a better describing of the NLO response, the fallowing relation can consider,

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_S)} + \beta_{RSA}I \tag{5}$$



Fig. 7. Open aperture Z-scan data of NZB glasses at a) 750 nm b) 800 nm and c) 850 nm. Open circles represent the experimental data while the solid lines represent the theoretical fits.

where, ' β_{RSA} ' is the reverse absorption coefficient (two-photon absorption), 'I' is the laser intensity and 'I_S' is the saturation intensity. In the above equation, the first term describing saturation absorption (SA) whereas second term corresponding to reverse saturable absorption (RSA). When only RSA kind of nonlinear absorption is present 'I_S' will be zero and ' β_{RSA} ' will be zero for the case of pure SA. By fitting the OA Z-scan data using equation (5) [solid lines in Fig. 7 (a–c)], the saturation intensities (I_S) were determined. Similar NLO results (SA) were

Table 3

Summary of the NLO coefficients obtained for different glasses studied in the present work: two photon absorption coefficient (β), nonlinear refractive index (n_2), linear absorption coefficient (α_0), saturation intensity (I_s).

Glass codes	1NZB	2NZB	3NZB
$\begin{aligned} \lambda &= 750 \text{ nm} \\ n_2 (m^2 W^{-1}) \times 10^{-16} \\ \alpha_0 (cm^{-1}) \\ \beta (mW^{-1}) \times 10^{-14} \\ I_S (Wm^{-2}) \times 10^{11} \\ \lambda &= 800 \text{ nm} \\ - (m^2 W^{-1}) \times 10^{-16} \end{aligned}$	$\begin{array}{c} -3.8 \pm 0.38 \\ 0.711 \\ 4.6 \pm 0.46 \\ 7.6 \pm 0.76 \\ 1.2 \pm 0.12 \end{array}$	$\begin{array}{c} -4.3 \pm 0.43 \\ 0.853 \\ 3.8 \pm 0.38 \\ 8.4 \pm 0.84 \\ 1.0 \pm 0.10 \end{array}$	-4.6 ± 0.46 1.091 3.6 ± 0.36 11.9 ± 1.19
$ \begin{split} & & \Lambda_2 \ (m^2 W^{-1}) \times 10^{-14} \\ & & \alpha_0 \ (cm^{-1}) \\ & & \beta \ (mW^{-1}) \times 10^{-14} \\ & & J_3 \ (Wm^{-2}) \times 10^{11} \\ & & \lambda = 850 \ nm \\ & & \Lambda_2 \ (m^2 W^{-1}) \times 10^{-17} \\ & & \alpha_0 \ (cm^{-1}) \\ & & \beta \ (mW^{-1}) \times 10^{-14} \\ & & I_5 \ (Wm^{-2}) \times 10^{10} \end{split} $	$\begin{array}{r} -1.2 \pm 0.12 \\ 0.685 \\ 5.2 \pm 0.52 \\ 1.4 \pm 0.14 \\ -2.6 \pm 0.26 \\ 0.664 \\ 7.2 \pm 0.72 \\ 3.9 \pm 0.39 \end{array}$	$\begin{array}{c} -1.9 \pm 0.19 \\ 0.822 \\ 4.6 \pm 0.46 \\ 2.8 \pm 0.28 \\ -4.1 \pm 0.41 \\ 0.796 \\ 8.4 \pm 0.84 \\ 4.6 \pm 0.46 \end{array}$	$\begin{array}{c} -2.8 \pm 0.28 \\ 1.06 \\ 8.1 \pm 0.81 \\ 6.5 \pm 0.62 \\ -8.0 \pm 0.8 \\ 1.043 \\ 10.12 \pm 1.01 \\ 6.2 \pm 0.62 \end{array}$

observed by Jagannath et al. in borate glasses doped with Au NPs at 800 nm under fs regime [9] and by Almedia et al. [10] in gold NPs doped heavy metal oxide (HMO) glass matrix after the heat treatment at 420 °C at the wavelength of 780 nm under fs regime for and also in lanthanum lead borate glasses embedded with gold NPs at the excitation of 532 nm under nanosecond (ns) regime after the heat treatment at 550 °C by Rajaramakrishna et al. [11]. As listed in Table 3, the value of 'Is' increases with respect to Na₂O concentration and the table suggest that 3NZB glasses possess high value Is compared to 1NZB and 2NZB. The values of I_S of present NZB glasses are found to be more comparable with those reported recently [9,10] and the I_S values are quite high compared to that of gold nanoparticles doped HMO glasses [10] and also that of gold nanoparticles doped lanthanum lead borate glasses [11]. It has been reported that, for Au NPs (or nanocrystals), the first excited transition which occurs at 670 nm (1.52 eV)is purely an intraband (sp \rightarrow sp) transition, the transition occurring at 450 nm (2.63 eV) is due to mixed intraband (sp \rightarrow sp) and interband (d \rightarrow sp) transitions. The intraband transition is the transition of free valence electrons close to the Fermi surface which can transit even with photons of low-energy, while the interband excitation requires higher energy photons and is the excitation of electrons to the conduction band from d-band [9,42]. In the present investigation the glass samples comprising of Au NPs are excited at 750 nm, 800 nm, 850 nm to measure the NLO properties, the energies ($\sim 1.65 \text{ eV}$, $\sim 1.55 \text{ eV}$ and $\sim 1.46 \text{ eV}$) of the excited wavelengths (750 nm, 800 nm and 850 nm, respectively) are very near to that of the energy required for the intraband (sp \rightarrow sp) transition within Au NPs and also while during the experiment the input peak intensity was 8.2×10^8 Wcm⁻² (nearly same for all the samples at all the wavelength at a range of \pm 0.9) which is not high. Therefore, it can be concluded that the SA type of nonlinear absorption observed for all the samples at wide spectral range from 750 nm to 850 nm is due to the intraband transition (i.e. from sp \rightarrow sp) within Au NPs. The sign and magnitude of nonlinear refraction have been measured using CA mode of Z-scan. Fig. 8(a) - 8(c) depict the CA Z-scan signatures of NZB glass samples at 750 nm, 800 nm and 850 nm respectively, in which the open circles represent the experimental data while the solid lines are theoretically fitted data. From Fig. 8 it is evident that the presence of a pre-focal transmission maximum followed by a post-focal transmission minimum (i.e., a peak-valley configuration) indicates nonlinear refraction is negative and the lensing effect would be of self-defocusing type. In fact, all NZB glasses were found to exhibit enhanced nonlinear refraction of negative type at all the excitations.

For evaluating the n_2 , the experimental CA Z-scan data point were fitted with equation (6) and the value was calculated using the relation (7) [9,43].



Fig. 8. Closed aperture Z-scan data of NZB glasses at a) 750 nm b) 800 nm c) 850 nm. Open circles represent the experimental data while the solid lines represent the theoretical fits.

$$T_{CA} = 1 - \frac{4\Delta\Phi_0(Z/Z_0)}{[1 + (Z/Z_0)^2][9 + (Z/Z_0)^2]}$$
(6)

where, 'Z' is the sample position, $Z_0 = \pi \omega \delta_{\lambda}^2$ is the Rayleigh Range and ' $\Delta \Phi_0$ ' be the difference in phase of the laser beam attributed to non-linear refraction.

$$n_2(m^2 W^{-1}) = \frac{|\Delta \Phi_0|\lambda}{2\pi I_{00} L_{\text{eff}}}$$

$$\tag{7}$$

where, 'Leff'- effective path length inside the sample of length 'L' and for 2 PA is $L_{eff} = \frac{1 - e^{\alpha 0 L}}{\alpha_0}$, 'I₀₀' be the peak intensity in the input laser beam and ' λ ' is excitation wavelength laser radiation used in the measurement. The same kind of negative nonlinear refractive indices also reported by Zhang et al. [44] for copper NPs in Na₂O-CaO-B₂O₃-SiO₂ glasses at 1550 nm with fs pulse excitation, Fangming et al. [45] for iron oxide NPs incorporated in mesoporous silica thin films at 1064 nm with picosecond (ps) excitation. Further, the nonlinear refractive indices of the present NZB glasses (can be seen from Table 3) are superior when compared with that of Au NPs doped HMO glasses [10]. Au NPs doped PbO–GeO₂ thin film [12], antimony orthophosphate glasses [46], silver NPs doped Bi₂O -B₂O₃-SiO₂ ternary glasses [47], copper NPs embedded sodium borosilicate glasses [48]. This enhancement in nonlinear refractive index of present glasses can be explained as follows. Recent reports suggest that the increase in refractive index (both linear and nonlinear) is due to the increase of density of NPs (or in turn increase of atomic concentration) in the glasses [9] and the atomic concentration is inversely related [relation found in Ref. [49] to the average molecular weight of the glass composition. Hence, the presence of HMO in above compared glasses the average molecular weight obviously is more as compared to present NZB glasses and therefore the Au atomic concentration or Au NPs density is more in the present NZB glass system (and less in compared glass systems) leading to an enhanced nonlinear refractive index.

From the applications point of view, the glasses possessing small nonlinear absorption (two-photon absorption) and large nonlinear refractive index are potential materials for ultrafast optical switches in optical fiber communications. The figure of merit can be used to decide the suitability of the optical switching characteristics; hence the figure of merit was determined using [50],

$$F = \frac{2\beta\lambda}{n_2} \tag{8}$$

where, F is the figure of merit, β is the two-photon absorption coefficient, λ is the wavelength of excitation and n_2 be the nonlinear refractive index. The 'F' for all the glass samples was measured and is found to be < 1 at all the excitation wavelengths suggesting that these glasses are suitable for optical switching applications. In the present case the values of β were found to be $\sim 10^{-14}$ m/W, which are significantly low whereas the typical values of n_2 were $\sim 10^{-16}$ m²/W.

It has been recently reported [22] that the presence of reducing agent in the glassy matrix effectively converts Au ions to Au MNPs by providing reduction condition in the glass matrix during the fabrication. Smithies et al. [37] have demonstrated that sodium acts as an alternative reducing agent, which forms stable Au MNPs of smaller size. In the present investigation the concentration of sodium is varied to investigate the effect of alkali on properties of Au NPs in borate glasses. Therefore, with increased sodium content in the glass matrix the density of Au NPs and/or Au atomic concentration is increased due to effective conversion and, hence, the saturation intensity (Is) and nonlinear refractive index (n_2) values are increased. However, the rate of increase of n_2 is less compared to rate of increase of I_s (refer Table 3) which suggests that Na₂O is also possibly contributing to nonlinear absorption. Whilst in the previous work [9] the concentration of gold doping was varied to analyse the effect of gold concentration on optical and NLO properties of Au NPs and it was observed the both I_S and n₂ were increased at nearly similar rate. From the data presented in the Table 3 it can be concluded that the values of saturation intensity (I_s) and nonlinear refractive indices (n_2) are higher at 750 nm when compared to those at 850 nm and 800 nm, because the 750 nm wavelength is close that the SPR band of Au NPs.

We did not observe any clusters in HR-TEM images of Au doped NZB glasses. The formation of clusters in the glasses follows two-step process: In a first step, metal ions are introduced in the glass matrix by either direct ion implantation or by the ion exchange or by direct melt quench methods. Subsequently, the glasses are heat treated by proper combination of treatments, including irradiation by either low-mass ion beams or electrons, heat treatments in reducing atmosphere, or pulsed laser irradiation [51]. In the present study the sodium in the glass composition forming stable Au NPs and further heat treatment (at 300 °C) was done to only remove thermal stresses. Hence the cluster formation is not possible in the present glasses. However, the physical mechanisms governing the cluster formation in the glasses are still under debate and need further investigations.

4. Conclusions

In summary, the gold NPs doped sodium zinc borate glasses with different concentration of sodium have been successfully fabricated using conventional melt quench technique. The influence of Na2O concentration on optical, thermal, structural and NLO properties have been studied and analyzed. XRD profiles of all the glasses presents the broad hump like amorphous peaks centered at 45° of 20 which discloses, all the glass samples are amorphous in nature. Since the concentration of gold in NZB glasses is low, the XRD profiles did not reveal any sharp peaks. The SPR absorption peak is slightly red-shifted from 577 nm to 593 nm with increase in Na_2O concentration from 10 mol% to 30 mol% respectively. The decreasing trend of band gap energies (both direct and indirect) with rise in sodium content in the glass composition is attributed to the enrichment the NBOs presence (with increase in Na₂O mol % in the composition) and by this means the absorption edge shifts to lower energies. The DSC measurements reveal that, the T_g is increased with sodium content. The absence of absorption band at 806 cm⁻¹ in FTIR spectra of all prepared glass samples suggesting the structural network of present glasses does not contain any boroxol rings. The fs NLO properties of the titled glasses have been studied at three different non-resonant wavelengths using the Z-scan technique. On the application side, the ultrafast NLO properties of present glasses suggest that the present NZB glasses containing gold NPs are superior candidates for nonlinear devices applications like optical switches, Q-switches, mode lockers (for use in the generation of ultrashort pulses) in the near-IR spectral regime.

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