Nanosecond Nonlinear Optical and Optical Limiting Properties of Eu$^{3+}$ Activated Borate Glasses Embedded with Silver Nanoparticles

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Abstract. Nonlinear optical and optical limiting attributes are evaluated at 532 nm using nanosecond laser pulses. The nonlinear coefficients such as nonlinear absorption and nonlinear refractive index values are increased with increase in AgNO3 concentration while the optical limiting threshold values showed a reverse trend. The increase in nonlinear optical properties in studied glasses with the Ag nanoparticles number density attributed to the local field effect stimulated by surface plasmon resonance of Ag nanoparticles when glasses are exposed to high energy radiation. The increase in nonlinear absorption and decrease in optical limiting threshold coefficients with AgNO3 concentration suggest the glasses containing high concentration of Ag nanoparticles are useful for designing the power optical limiters for functioning at the visible region under nanosecond regime.

INTRODUCTION

Rare Earth (RE) ions doped vitreous materials are greatly studied by many materials scientist to design diverse photonic materials which includes the optical amplifiers, optical fibers, solid state lasers, optoelectronic devices, sensors, display devices and many more$^1$. Incorporating the of RE ions to vitreous host and tuning the high optical nonlinearities has been well explored route in recent years$^1–3$. This is because, the polarizabilities of RE ions strongly contribute for the enhancement of nonlinear optical (NLO) factors of glasses$^2,4$. The optical limiting (OL) materials restricts the transmitted light intensity below the material damage threshold at great laser energy and remains transparent under less energy irradiation. Basically, the OL materials predominantly exhibit a third–order NLO property and depicts the ideal benefit such as low limiting thresholds, great damage thresholds, high linear transmittance and broadband spectral protection$^5,6$. Therefore, it is vital to study the third–order NLO properties of RE doped glasses to develop the next generation photonic devices, particularly to develop the protective materials.

Usually, the absorption cross-section of Eu$^{3+}$ ions is too faint which hinders their practical use of Eu$^{3+}$ activated glasses in NLO device applications. However, the co–doping of metal nanoparticles (MNPs) into RE doped glasses can effectively modify the local field near the Eu$^{3+}$ ions through surface plasmon resonance (SPR) thereby causes the enhancement in optical nonlinearity of the parent glass. Among different glasses, the borate based glasses are of significant interest because of their good thermal stability, low melting point, and good solubility of (RE) ions$^4$. 
EXPERIMENTAL AND CHARACTERIZATION DETAILS

The borate glasses bearing the composition 10Sb$_2$O$_3$–20Na$_2$O–69B$_2$O$_3$–1EuO$_3$–$x$AgNO$_3$ ($0 \leq x \geq 0.8$ mol %, in steps of 0.2 mol %), were prepared via conventional melt quenching. The detailed procedure followed for preparing the glasses has been explained in our earlier report. The samples used for characterizations were labelled as SNBEuAg$_x$ based on the AgNO$_3$ concentration present in the glass compositions, in the codes the $x$ represent the concentration of AgNO$_3$ incorporated in the glass compositions.

The occurrence and geometric distribution of silver NPs was confirmed through FEI Technai G2 20 transmission electron microscope (TEM) measurements. NLO properties such as nonlinear absorption and nonlinear refractions respectively were studied using Z–scan technique in open aperture (OA) and closed aperture (CA) configurations. The detailed procedure followed for measuring the NLO property using Z–scan experiments are explained in our earlier work.

RESULTS AND DISCUSSION

Figure 1 (a) shows the TEM image of SNBEuAg$_{0.4}$ glass sample and the corresponding histogram representing the particle size distribution in glass is illustrated in Figure 1 (b). The mean particle size of Ag NPs was estimated through ImageJ software. Figure 1 revealed the presence of more or less spherical shaped and homogenously distributed Ag NPs in the glass sample. From the histogram, the average particle sizes of the Ag NPs in SNBEuAg$_{0.4}$ glass is found to be $\sim 7$ nm. However, a very minimal number of non–spherical shaped silver NPs are evidenced in TEM images.

The standard reduction potentials ($E^0$) values of multi valent elements in glass melts may be different from those in aqueous solutions and dependent on temperature. Since $E^0$ values for simple glass systems at high temperature are not available in literature, therefore, the room temperature values for simple systems at equilibrium with air as reference were used here to explain the plausible mechanism of selective thermochemical reduction in Ag$^+$ to Ag$^0$ by Sb$^{3+}$ and not reduction of Eu$^{3+}$ by Sb$^{3+}$\textsuperscript{8,12}.

Thus, Sb$^{3+}$ is predicted to reduce Ag$^+$ to Ag$^0$ by itself being oxidized to Sb$^{5+}$. Besides Sb$^{3+}$ has an intrinsic character to get oxidized to Sb$^{6+}$. Here the thermo chemical reduction reaction Sb$^{3+} + 2$Ag$^+ \rightarrow$ Sb$^{6+} + 2$Ag$^0$ ($E^0 = 1.02$ V, $\Delta G = -nE^0F = -197$ kJ) has positive reduction potential ($E^0$) and negative free energy ($\Delta G$) suggesting this reaction is spontaneous and feasible reduction reaction. While, the other reaction 3Sb$^{3+} + 2$Eu$^{3+} \rightarrow 3$Sb$^{5+} + 2$Eu$^0$ ($E^0 = -5.93$ V, $\Delta G = -nE^0F = 3334$ kJ) would have a negative reduction potential along with positive free energy manifesting this reaction is non spontaneous and thermodynamically not feasible. Thus only Ag$^+$ is reduced and Eu$^{3+}$ is not.

FIGURE 1: (a) TEM image of SNBEuAg$_{0.4}$ glass, (b) histogram representing the Ag NPs size distribution in SNBEuAg$_{0.4}$ glass.
The representative OA and CA Z-scan data of SNBEuAg0 glass are depicted in inset of Figure 2 (a) and 2 (b) respectively. The OA Z-scan profile suggests the reverse saturable absorption (RSA) nonlinear property present in the glasses used in the current investigation. Similar features were observed in all SNBEuAgx glasses. The number of photons absorbed for the evidenced optical nonlinearity was calculated by fitting the OA Z-scan data with the nonlinear absorption equation mentioned reference\(^1\). Experimental OA Z-scan data of SNBEuAgx glasses were fitted well with two photon absorption (2PA) equation, suggest the absorption nonlinearity in the studied glasses is due to 2PA. Signature of CA Z-scan data of SNBEuAg0 glasses displayed in inset of Figure 2 (b) representing the presence of positive nonlinear refraction \((n_2 > 0)\), the similar features have been observed in all SNBEuAgx glasses. This refraction nonlinearity could be ascribed to self-focusing effect\(^1\). The nonlinear refractive index \((n_2)\) values were retrieved by following the procedure mentioned in reference\(^9\). In Figure 2 insets, the symbols represent the experimental measured Z-data points while the solid lines represent theoretical fits. The variation of 2PA coefficient \((\alpha_2)\) and nonlinear refractive index \((n_2)\) values with respect to AgNO\(_3\) concentration is displayed in Figure 2 (a) and 2 (b) respectively. The errors bars showed in the plots for the evaluated values occur mainly due to contrast in the estimation of laser beam waist at focal point and the resulting errors in peak fluencies along with fitting errors. From the Figure 2 it is clear that both \(\alpha_2\) and \(n_2\) are increased with respect to AgNO\(_3\) concentration. This increase trend of NLO coefficients can be explained as follows, the third-order NLO susceptibility \((\chi^{(3)})\) of MNPs containing glasses is strongly related to local electric field \((E_{loc})\) and hyper polarizability \((\alpha(3))\) according to the eqn. mentioned below\(^10\),

\[
\chi^{(3)}(-\omega, \omega_1, \omega_2, \omega_3) = \frac{L(\omega_1)L(\omega_2)L(\omega_3)}{26} \sum_i {N_i} \alpha_i^{(3)}
\]

These oscillations induce a confined electromagnetic field near the MNPs which induced the local electric field around the NPs with respect to the incident field due to the focus of light\(^8,10,13\). Because of this induced local electric field the third-order NLO susceptibility \((\chi^{(3)})\) is improved as per equation 4. Further, this induced electric field around the Eu\(^{3+}\) ions lying in the close proximity of MNPs increases the distortion of outer 4\(^{th}\) valence electrons of Eu\(^{3+}\) produces greater charge displacements thereby resulted in great improvement in optical nonlinearities of glasses. The improvement in NLO properties is also due to the fact that, the Ag NPs containing glasses demonstrated Ag NPs SPR absorption peak centred at 422 nm which sheds from 410 to 505 nm in linear optical
absorption spectra (not shown here). Therefore, the weak contribution from resonant and energy transfer mechanisms cannot be ignored for evidenced improved optical nonlinearities.

The optical limiting (OL) materials are important in designing the laser safety and pulse shaping devices, etc.\textsuperscript{14}. In OL materials, the OL property occurs when the input energy goes beyond certain threshold value (OL threshold). The OL threshold is vital factor to evaluate the performance OL materials. From OA Z–scan, the optical limiting patterns of studied glasses extracted, results are presented in Figure 3 (a). The Figure 3 (b) represent the attenuation in OL threshold values with respect to AgNO\textsubscript{3} content, reveal that the OL threshold decreased as AgNO\textsubscript{3} doping concentration increased in the composition.

The increase in 2PA and decrease in OL threshold values with respect to AgNO\textsubscript{3} concentrations suggest the high Ag NPs embedded glasses are useful for designing the optical limiters. Nonetheless, the utilization of the vitreous materials for optical limiting device applications also validated by calculating the figure of merit (FOM) values. All the studied glasses possess the FOM > 1. Which further supports the utilization of studied glasses in designing the OL devices.

\textbf{CONCLUSIONS}

The Eu\textsuperscript{3+} activated borate glasses embedded with different concertation of Ag NPs were prepared. TEM image confirmed the presence, shape and size of the Ag NPs. The OA and CA Z–scan profiles revealed the presence of positive optical nonlinearity (RSA signature in OA and valley–peak signature in CA) in all the studied glasses. OL threshold values demonstrated decrease trend with respect to AgNO\textsubscript{3} content in the glass composition. The increase in NLO properties in studied glasses with respect to Ag NPs concentration attribute to local electric field induced by SPR of Ag NPs when they are exposed to high energy radiation. The increase in NLO coefficients (particularly 2PA) and decrease in OL threshold values with AgNO\textsubscript{3} concentration recommend the high Ag NPs containing glasses (here SNBEuAg0.8 glass) are beneficial for the fabrication of the optical limiters for functioning at visible region under ns regime.

\textbf{REFERENCES}