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## 1. Introduction

In the present era, the nonlinear optical (NLO) properties of rare-earth (RE) containing oxide glasses with an instant response

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- $\dagger$  The primary author (G. J.) wishes to dedicate this article to the memory of his
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Alkali borate glasses activated with trivalent europium ions and rooted with gold (Au) nanoparticles (NPs) were synthesised through a melt quenching process involving a selective thermochemical reduction and their applicability as photonic materials was assessed in detail. Non-linear optical (NLO) measurements were performed using a *Z*-scan approach in the wavelength range of 700–1000 nm. The open aperture *Z*-scan signatures for the Eu<sup>3+</sup>-containing glasses embedded with and without the Au NPs established a reverse saturable absorption (RSA) at all of the studied wavelengths ascribed to the two-photon absorption (2PA). Surprisingly, the nonlinear optical absorption switched to a saturable absorption (SA) with an increase in the concentration of AuCl<sub>3</sub>. With the incorporation of the Au NPs, the UV excited photoluminescence (PL) intensity of the Eu<sup>3+</sup>-doped glasses increased first as a consequence of the local field enhancement by the Au NPs, and subsequently decreased at a higher concentration of AuCl<sub>3</sub> due to the reverse energy transfer from the Eu<sup>3+</sup> ion to the Au<sup>0</sup> NPs. The electronic polarization effect of the host glass enhanced the <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>4</sub> transition intensity on the incorporation of the gold NPs owing to the gold NP-embedded glasses showing a deep-red emission. The NLO and PL studies suggested that the investigated glasses containing a 0.01 mol% of AuCl<sub>3</sub> is practically appropriate for photonic applications.

to the electric fields of a light beam are very crucial for optical telecommunication, data storage and information processing, optical computing, optical limiters, solid-state lasers, infrared-tovisible converters, displays, sensing and other photonic devices.<sup>1-3</sup> To this end, borate glasses were precisely employed due to their low melting and processing temperatures. Also, borates are superior candidates in NLO applications compared to other commonlyused NLO materials.<sup>4,5</sup> Nevertheless, the addition of alkali ions, such as sodium, to borate glasses provides UV transparency along with a relatively high optical damage threshold<sup>5</sup> and improves the mechanical and chemical stability as well as the glass-forming ability.<sup>6,7</sup> Owing to these benefits, alkali-containing borate glasses are the best candidates for deep-ultraviolet (UV) NLO materials and are being utilised for practical applications in semiconductor lithography, nano-micro mechanical machining and biological gene engineering.<sup>5</sup> In addition, among the systems used in photonics, the use of glasses as dielectric matrix hosts for RE ions has additional advantages, such as a high transparency in selective electromagnetic fields, a high mechanical and chemical strength, the possibility of producing devices on several shapes such as blocks, lenses and fibers as well as the absence of metal-ligand interactions, which would cause a



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quenching process due to the high energy stretching vibrations.<sup>8</sup> Furthermore, based on the various photonic device requirements, the optical properties of glasses can be tuned by selecting a suitable host matrix, varying the RE concentration and the pumping wavelengths, *etc.*<sup>3</sup>

The exploration of lanthanide-containing materials exhibiting NLO properties has become an emerging field of research. Recently, Santos et al.9 and Nanda et al.10 analysed the impact of RE ion doping in borate glasses and observed their consequences on NLO properties. From the observations, they demonstrated a significant contribution of polarizability from the RE ions on the enhancement of the NLO properties. It is practically essential to develop materials for nonlinear device applications at the spectral regions of lasers that are commercially-available. In addition, lanthanide ions, particularly Eu<sup>3+</sup>, yield decent nonlinear coefficients at non-resonant wavelengths and are preferred for their practical applications. Among all the RE ions,  $Eu^{3+}$  has been greatly proven as a suitable activator for red photoluminescence (PL) in both glasses and crystalline materials.11 The intrinsic excitation bands of Eu<sup>3+</sup> are present near the maximum quantum efficiency of near-UV and blue LEDs. Hence, they are potential candidates for LED-pumped converters. The PL spectrum of Eu<sup>3+</sup> was characterized by various sharp lines in the orange to red spectral region due to the intra-configurational 4f  $\rightarrow$  4f parity-forbidden electric transitions from the non-degenerate <sup>5</sup>D<sub>0</sub>. The local environment around Eu<sup>3+</sup> was not sensitive to the magnetic-dipole, which allowed for the transition of Eu<sup>3+</sup>:  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  (orange). However, the electric-dipole, which allowed for the transition of Eu<sup>3+</sup>:  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  (red), was strongly affected.<sup>11–14</sup> Moreover, the f electrons of the lanthanides were sensitive to the external laser electric field and contributed to the hyperpolarizability, thereby enhancing the NLO activity.<sup>15</sup> Therefore, it is necessary to analyse the optical nonlinearities of Eu<sup>3+</sup>-containing borate glasses in the near IR region.

Normally, the optical absorption coefficient of Eu<sup>3+</sup> is very small in the ultraviolet (UV) range, which results in a lowefficiency emission under UV excitation<sup>2</sup> and therefore, limits their versatility in many applications. However, the incorporation of noble metal nanoparticles (MNPs) into glass hosts can effectively alter the local field at the vicinity of the Eu<sup>3+</sup> ions through surface plasmon resonance (SPR).<sup>3</sup> Also, the overlapping of the SPR band and the PL of the RE ions is essential for the improvement of the luminescence of the RE ions persuaded by the noble MNPs.<sup>16</sup> Usually, the SPR band of the Ag NPs coincides with the absorption wavelength of the Eu<sup>3+</sup> ions and the SPR band of the gold (Au) NPs is overlaid with the luminescence wavelength of Eu<sup>3+</sup> ions.<sup>16</sup> Hence, a maximum enhancement in the Eu<sup>3+</sup> luminescence was expected in the glasses containing the Au NPs compared to those for the Ag NPs since the Eu<sup>3+</sup> emission transitions could have been further affected due to the local field effects and energy transfer processes involving the Au NPs. The local field amplitude enhancement due to the SPR of the NPs was considered as an acceptable route for the RE luminescence enrichment. A second realisable route for luminescence improvement included the absorption of light by the NPs and the transfer of energy to the RE ions.<sup>17</sup> Since it is known that the absorption coefficient of the NPs was higher compared to the RE ion, this luminescence excitation cause may be more convincing in some investigations. However, various hypothetical ideas are being considered to describe the effect of the MNPs on the emission properties of the RE ions.<sup>18–22</sup>

Usually, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition intensity is enhanced with respect to the following: (i) the local glass network structure, (ii) the RE ion concentration and (iii) the MNP concentration along with the temperature treatment schedule.<sup>2,3,23-25</sup> Because of the weak features, most studies related to Eu<sup>3+</sup>-emission properties do not concentrate on the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition. Nevertheless, the significant role of the dominant emission intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition has not been explored to date. It has been mentioned in very few reports that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition of the Eu<sup>3+</sup> ion is dominant when the ligands of the Eu<sup>3+</sup> ion have high values of polarizabilities, for example, gold nano-particle ligands.<sup>14,26-28</sup> Furthermore, in addition to this constructive approach of the MNP inclusion in glasses for luminescence improvement of RE ions, an attempt was also made to enhance the NLO coefficients of RE-doped glasses. These MNPs improved the NLO properties through the local field effect due to a collective oscillation of the electron cloud on the nanoparticle surface after excitation with higher wavelengths compared to their particle size. Also, smaller NPs with sharp edges contribute more to the NLO effects as the local field increases the hyperpolarizabilities. The NLO effects are greater as the local field increases the hyperpolarizabilities.<sup>29</sup> However, there are very few reports available in the literature to support this.<sup>29,30</sup> To shed further light on this aspect, we attempted to explain the mechanism involved in the enhancement of nonlinear coefficients for RE-doped glasses embedded with Au NPs.

Because of the above evidence, an attempt was made to understand the impact of gold NPs on the NLO and photoluminescence (PL) attributes of the Eu<sub>2</sub>O<sub>3</sub> containing (0.5 mol%)  $5Sb_2O_3-25Na_2O-70B_2O_3$  glasses. Furthermore, we explained the enhancement in the intensity of the  ${}^5D_0 \rightarrow {}^7F_4$  transmission of the Eu<sup>3+</sup> as a function of the AuCl<sub>3</sub> concentration. It was illustrated that due to a mild thermal reducing agent (Sb<sup>5+</sup>/Sb<sup>3+</sup>,  $E_o = 0.65$  V), the added heavy metal oxide (Sb<sub>2</sub>O<sub>3</sub>) facilitated the *in situ* selective reductions of gold from its Au<sup>3+</sup> to Au<sup>0</sup> state <sup>31</sup> in a single-step during the melting glass composition.<sup>32</sup> This provides a straightforward, inexpensive strategy for the preparation of nano-photonic materials.

## 2. Experimental

#### 2.1. Preparation of glasses

The alkali borate oxide glasses were synthesised based on the molar composition,  $5Sb_2O_3-25Na_2O-69.5B_2O_3-0.5Eu_2O_3-xAuCl_3$  (x = 0 to 0.02 mol%), through a melt quenching method as reported elsewhere.<sup>33,34</sup> The fabricated glass systems were activated with the Eu<sup>3+</sup> ions and embedded with various

concentrations of the Au NPs. The fabricated samples were coded as SNBE, SNBEA-1, SNBEA-2 and SNBEA-3 for the glasses containing 0, 0.005, 0.01 and 0.02 mol% of AuCl<sub>3</sub>, respectively (along with 0.5 mol% of  $Eu_2O_3$ ).

#### 2.2. Characterization techniques

In order to confirm the glassy character of the prepared glass samples and also to identify the gold NP phases, X-Ray Diffraction (XRD) scans were recorded using a Rigaku Ultima-IV X-Ray diffractometer with a resolution of 0.01°. A Carl Zeiss scanning electron microscope (SEM) operating at 15 kV and equipped with an energy dispersive X-ray (EDX) detector was used for the elemental analysis. Glasses embedded with the Au NPs with a flat surface were used in the EDX measurements. The linear optical absorption data were collected at room temperature by utilizing a PerkinElmer Lambda-35 Ultra Violet-visible (UV-Vis) spectrometer. The refractive index measurements were performed using an Abbe's refractometer. For these measurements, monobromonapthalene was used as the contact layer between the sample and the prism of the refractometer. A sodium vapour lamp emitting at a wavelength of 589.3 nm (D line) was used as a source of light. The existence of the gold NPs was confirmed through transmission electron microscope (TEM) measurements using a FEI Technai G2 20 TEM. For the TEM measurements, the glass samples containing the gold NPs were finely crushed to obtain a homogeneous powder. The PL spectra were recorded on a fluorescence spectrophotometer (HORIBA JOBIN YVON, Fluorlog). The Z-scan approach was utilized for assessing the absorption and refraction optical nonlinearities of the prepared glasses in open aperture (OA) and closed aperture (CA) modes, respectively. In the Z-scan approach, the output transmission of the glass samples were recorded as a function of the input intensity of the laser light. The glass sample was displaced along the propagation axis (Z-axis) to vary the fluence of the laser beam, which was focused by using a plano-convex lens. The output transmission was collected at different positions (Z) of the sample based on the beam focus. Based on the position (Z) of the sample, the samples experienced a different laser fluence with the highest or lowest fluence at the focal point (Z = 0). Furthermore, the NLO characterizations were performed in the spectral range of 700-1000 nm by utilizing 150 femtosecond (fs) laser pulses fired at a 80 MHz repetition rate from a Ti:Al<sub>2</sub>O<sub>3</sub> laser (Chameleon, M/s Coherent). In all of the Z-scan experiments, the input peak intensities  $(I_{00})$  were in the range of 8  $\times$  10<sup>8</sup>–11  $\times$  10<sup>8</sup> W cm<sup>-2</sup>. Optically polished glass samples of 1 mm in thickness and 10 mm in diameter were used for the optical, luminescence and nonlinear characterizations.

### 3. Results and discussion

#### 3.1. XRD, optical absorption and TEM studies

The XRD profiles of all the obtained glass samples depicted in Fig. 1 exhibited two broad humps between  $20^{\circ}$  and  $50^{\circ}$  without any crystalline peaks, which indicated the glassy nature. No traces of XRD peaks related to Au NPs were observed in the AuCl<sub>3</sub> embedded glasses because of the low concentration



Fig. 1 X-Ray diffraction patterns of the  ${\rm Eu}^{3+}$  containing SNBE and SNBEA glasses.

of AuCl<sub>3</sub> (ranges from 0.005 to 0.02 mol%). However, to check the chemical composition and the quantitative atomic percentage of the compositional elements present in the Au-doped glasses, EDX analyses were performed on all of the gold containing samples. The EDX analysis (Fig. S1, ESI‡) confirmed the presence of Au in the AuCl<sub>3</sub> doped glasses. The results of the EDX analysis are provided in the ESI.‡

The room temperature optical absorption spectra of the obtained glasses are shown in Fig. 2(a). Fig. 2(b) presents the absorption spectrum of the SNBE glass (doped with 0.5 mol% of  $Eu_2O_3$ ) along with the band assignments. Nine absorption peaks were identified, which were attributed to the 4f-4f electronic transitions for the  $Eu^{3+}$  ion from the ground  $^7F_0$  and thermally inhabited  $^7F_1$  states to the different excitation levels.<sup>35,36</sup>



Fig. 2 (a) Optical absorption spectra of  $Eu^{3+}$  singly and gold NP, co-doped, alkali borate glasses. (b) The optical absorption spectrum of  $Eu^{3+}$  (0.5 mol%) containing SNBE glass along with band assignments.

The absorption spectra of the gold-doped glasses exhibited a broad and characteristic SPR band for the Au<sup>0</sup> NPs at 567 nm, which was ascribed to the transitions of the interband type.<sup>37</sup> Because the SPR band for the Au NPs ranged from 490 to 700 nm, the characteristic  ${}^7F_1 \rightarrow {}^5D_3$ ,  ${}^7F_0 \rightarrow {}^5D_1$  and  ${}^7F_1 \rightarrow {}^5D_1$  absorption peaks of Eu<sup>3+</sup> positioned at 415, 525 and 532 nm, respectively, could not be revealed. From Fig. 2(a), it could be seen that the absorption range and intensity of the SPR peak for the gold NPs were enhanced with AuCl<sub>3</sub> doping. The maxima of the SPR band ( $\lambda_{max}$ ) experienced a regular red-shift with an unequal tail that extended up to 750 nm with the increase in the Au doping concentration from 0.005 to 0.02 mol%.

According to Mie's theory,<sup>38</sup> the average radii, '*R*', of the embedded NPs is calculated using the full-width at half maximum (FWHM,  $\Delta\lambda$ ) of the SPR absorption peak,<sup>39</sup>

$$R = \frac{V_{\rm f} \lambda_{\rm max}^2}{2\pi C \Delta \lambda} \tag{1}$$

where the Fermi velocity of the electrons is the  $V_{\rm f}$  (in bulk gold,  $V_{\rm f} = 13.82 \times 10^5 {\rm m s}^{-1}$ ),  $\Delta \lambda$  is the FWHM of the SPR absorption peak for the gold NPs and  $\lambda_{\rm max}$  is SPR absorption maxima, which is dependent on the size and the shape of the MNPs as well as the medium in which the MNPs were embedded. Furthermore, the position and shape of the SPR peak is sensitive to the index of refraction of the medium containing the MNPs. They are related as the following:<sup>40</sup>

$$\lambda_{\max} = \lambda_{\mathrm{P}} (1 + 2n^2)^{1/2} \tag{2}$$

where, *n* is the refraction index of the glass samples and  $\lambda_p (2\pi c/\omega_p)$  is the bulk plasmon wavelength (136 nm for gold).<sup>41</sup> The *n* values of the prepared glass samples increased from 1.627 to 1.642 with the increase in the concentration of the gold NPs as presented in Table 1. The increase in the *n* values with the increase in the concentration of the gold NPs validated the *n* values obtained from the absorption spectra (Section S2 in ESI‡). Theoretical calculations were performed using eqn (1) to estimate the particle sizes of the Au<sup>0</sup> NPs in the studied glass samples. The particle sizes were found to be 3.89 nm, 5.52 nm and 8.19 nm

for the SNBEA-1, 2 and 3 glasses, respectively. The calculated particle sizes are presented in Table 1.

Fig. 3 illustrates the TEM images and the respective histograms of the prepared gold NP-embedded glasses in order to understand the distribution of the Au NPs. The mean particle size of the gold NPs was calculated using ImageJ software. Fig. 3 revealed the existence of spherically-shaped and homogeneously distributed gold NPs in the investigated glasses. From the histograms, the average sizes of the gold NPs in the SNBEA-1, 2 and 3 glass samples were calculated to be  $\sim$  3.62 nm,  $\sim$  5.69 nm and  $\sim$  8.26 nm, respectively (Table 1). These values corroborated with the values measured by Mie's theory. However, a minimal amount of non-spherically-shaped Au NPs was also observed in the TEM images. Table 1 indicated that the particle size of the gold NPs increased from 3.62 nm to 8.26 nm with the increase in the Au concentration from 0.005 to 0.02 mol%, respectively. This observed phenomenon could have been due to two possible mechanism: (i) an Ostwald ripening process: where small atoms or small clusters of atoms diffuse from smaller to larger NPs, and (ii) a nanoparticle migration and coalescence occurred at a higher concentration of the Au NPs.<sup>42</sup> From Table 1, it was obvious that the particle sizes estimated from the TEM micrographs were in good agreement with those estimated using the Mie theory.

The concentration of Au (atoms per cm<sup>3</sup>) and Eu<sup>3+</sup> (ions per cm<sup>3</sup>) along with the inter-nuclear properties (*i.e.*,  $d_{Au-Au}$ ,  $d_{Au-Eu}$ ,  $d_{Eu-Eu}$ ) were estimated using the relationships suggested in ref. 43 as shown in Table 1. Table 1 also indicated that the Au atomic concentration was enhanced with the increase in the gold doping level, which was again responsible for the increase in the intensity of the SPR absorption peak for the gold NPs.<sup>44</sup> From Fig. 2(a), it was shown that the maxima of the SPR band for the Au NPs ( $\lambda_{max}$ ) shifted towards the longer wavelength side (red-shift) as a function of the AuCl<sub>3</sub> concentration in the glass composition, which was due to the growth of the particle size for the Au<sup>0</sup> NPs caused by the Ostwald's ripening process<sup>45</sup> as evidenced from the TEM images and also from the Mie theory. From Fig. 2(a) it was observed that the SPR band of the Au<sup>0</sup> NPs gradually broadened from the gold doping due to the decrease in

Table 1         Physical and inter-nuclear properties of the studied glasses							
Properties	SNBE	SNBEA-1	SNBEA-2	SNBEA-3			
Physical properties							
Average molecular weight, $M$ (g mol <sup>-1</sup> )	80.219	80.235	80.253	80.287			
Density, $\rho$ (g cm <sup>-3</sup> )	2.564	2.486	2.421	2.388			
Molar volume, $V_{\rm m}$ (cm <sup>3</sup> mol <sup>-1</sup> )	31.286	32.274	33.148	33.621			
Refractive index, n	1.622	1.627	1.638	1.642			
$Eu_2O_3$ concentration (mol%)	0.5	0.5	0.5	0.5			
Concentration of AuCl <sub>3</sub> (mol%)	—	0.005	0.01	0.02			
Molar refractivity, $R_{\rm M}$ (cm <sup>-3</sup> )	11.018	11.439	11.913	12.143			
Electronic polarizability, $\alpha$ (Å <sup>3</sup> )	4.367	4.533	4.721	4.812			
Inter-nuclear properties							
$Eu^{3+}$ ion concentration (×10 <sup>22</sup> ions per cm <sup>3</sup> )	1.037	0.996	0.998	1.045			
Position of SPR peak of gold (nm)	—	567	573	581			
Au atoms concentration, $N(\times 10^{20} \text{ atoms per cm}^3)$	—	0.996	1.997	4.183			
Au–Au interparticle spacing, $d_{Au-Au}$ (nm)	—	2.19	1.737	1.358			
$Eu^{3+}-Eu^{3+}$ distance $(d_{Eu-Eu})$ (Å)	4.663	4.726	4.723	4.652			
$Eu^{3+}$ -Au distance (Å)	—	4.711	4.692	4.591			
Average size of Au NPs calculated by applying Mie theory (nm)	—	3.89	5.52	8.19			
Average size of Au NPs estimated from TEM images (nm)	—	3.62	5.69	8.26			



Fig. 3 TEM micrographs of SNBEA glasses embedded with different concentrations of Au NPs and their corresponding histograms representing the size distribution of the Au NPs.

the Au-Au interparticle spacing in the glass.<sup>46</sup> As a consequence, there was an effective surface-plasmon coupling among the closely-spaced Au NPs, resulting in a significant red-shift in the plasmon band. This finding suggested an increase in the localized electric field.<sup>46,47</sup> From Fig. 2, it was noticed that the amplitude of the SPR peak for the Au NPs was enhanced with respect to the AuCl<sub>3</sub> doping, which clearly suggested that more Au<sup>3+</sup> ions were reduced to Au<sup>0</sup> with the increase in the doping concentration of AuCl<sub>3</sub>.<sup>29</sup> Nonetheless, the dependence of the SPR peak for the Au NPs on the dielectric environment could not be ruled out since the  $\lambda_{\rm max}$  of the Au NPs had a direct correlation with the refractive index of the host medium embedded with the MNPs according to eqn (2). Therefore, the increase in the refractive index of the samples as a function of gold doping observed from Table 1 was attributed to the size and also the number density of the Au NPs. It was reported that the incorporation of the Au NPs in the glass matrix resulted in a large scale disruption in the network through the conversion of bridging oxygens (BOs) to non-bridging oxygens (NBOs) in the glass.<sup>45</sup> The creation of the NBOs contributed to a larger polarizability over the covalent bonds of the BOs by providing a higher refractive index.<sup>45</sup> Therefore, the increase in the refractive index values with the increasing incorporation of AuCl<sub>3</sub> in the present glasses was attributed to the creation of NBOs.48,49

#### 3.2. Nonlinear optical (NLO) measurements

To elucidate the effect of the Au NPs on the NLO properties of the Eu<sup>3+</sup>-doped glasses, the absorption and refraction NLO

characteristics were evaluated through OA and CA Z-scan configurations, respectively. The OA Z-scan plots of the studied glasses at all of the excitation wavelengths (700 nm, 800 nm, 900 nm and 1000 nm) are depicted in Fig. 4(a). Irrespective of the excitation wavelength, all of the glasses (except SNBEA-3) demonstrated a decrease in transmittance as they approached the focus point (Z = 0) and depicted a minimum at the focus point in the OA mode. This indicated a characteristic signature of (valley at focus) a reverse saturable absorption (RSA) type of nonlinearity [Fig. 4(a)]. The SNBEA-3 glass exhibited a saturable absorption (SA) nonlinearity (showed a maximum transmittance at the focus point in the OA mode). The CA Z-scan curves for all of the glasses demonstrated a peak following the valley configuration on the transmittance signal as displayed in Fig. 4(b), which represented the positive refraction nonlinearity and was attributed to a self-focusing effect.

To evaluate the effect of the Au NPs on nonlinear refraction, the CA Z-scan data were fitted with the following equation.<sup>34</sup>

$$T_{\rm CA} = 1 \pm \frac{4\Delta \Phi_0(Z/Z_0)}{\left[1 + (Z/Z_0)^2\right] \left[9 + (Z/Z_0)^2\right]}$$
(3)

where,  $\Delta \Phi_0$  is the phase difference of the laser beam that usually occurs because of a refraction nonlinearity, *Z* is the sample position,  $Z_0$  is the Rayleigh range  $[Z_0 = \pi \omega_0^2 / \lambda]$ ,  $\omega_0$  is the



**Fig. 4** (a) Open aperture *Z*-scan transmittance and (b) closed aperture *Z*-scan transmittance of  $Eu^{3+}$  singly and gold NP, co-doped, alkali borate glasses. In the figure, the symbols are representing the experimentally-measured data and the solid lines are indicating the theoretical fits to the measured data.

beam waist at the focus point (Z = 0) and  $\lambda$  is the excitation wavelength. The nonlinear refractive index  $(n_2)$  was evaluated using

$$n_2 = \frac{|\Delta \Phi_0|\lambda}{2\pi I_{00} L_{\rm eff}} \tag{4}$$

where  $L_{\text{eff}}$  is the distance travelled (path length) by the laser beam in the sample of length, *L*.  $I_{00}$  is the fluence of the laser beam at Z = 0.

To evaluate the magnitude of the nonlinear absorption coefficient, we considered the following equation for multiphoton absorption  $(MPA)^{34}$ 

$$T_{\text{OA}}(nPA) = \frac{1}{\left[1 + (n-1)\alpha_n L_{\text{eff}} \left(I_{00} / \left(1 + (Z/Z_0)^2\right)\right)^{n-1}\right]^{1/n-1}}$$
(5)

where  $\alpha_n$  is the MPA coefficient (*n* being the nonlinear absorption order, *i.e.*, n = 2 for 2PA; n = 3 for 3PA, *etc.*) and  $L_{\text{eff}}$  is the efficient path length travelled by the laser beam inside the sample length of *L*. For the case of 2PA, the  $L_{\text{eff}}$  was considered as  $L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$ . The OA *Z*-scan data of the SNBE and SNBEA (except SNBEA-3) glasses measured at different near IR excitation wavelengths fitted well with n = 2 in eqn (5). The data and fits are shown in Fig. 4. It was evident that the 2PA absorption was responsible for the observed nonlinearity in these glasses. The SNBEA-3 glass demonstrated a SA nonlinearity at excitations in the near IR region.

To understand the NLO effect in detail, the intensitydependent nonlinear absorption coefficient,  $\alpha(I)$ , was measured, which is given by<sup>34</sup>

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_{\rm S})} + \beta_{\rm RSA}I \tag{6}$$

where, ' $\beta_{RSA}$ ' is the nonlinear absorption coefficient (2PA or 3PA, *etc.*), *I* is the intensity of the laser radiation and *I*<sub>S</sub> is the saturation intensity. The physical significance of eqn (6) is that the first term explains the SA type of nonlinearity, while the

second term describes the RSA. The value of the ' $I_{\rm S}$ ' will be zero if only a RSA kind of optical nonlinearity is present in the samples, whereas the ' $\beta_{\rm RSA}$ ' will be zero if only SA is present in the samples. By fitting the OA Z-scan data for the SNBEA-3 glasses at near IR excitations using eqn (6), the saturation intensity ( $I_{\rm S}$ ) values were determined. The real and imaginary parts along with the total nonlinear susceptibility,  $\chi^{(3)}$ , were also evaluated using the standard relationship.<sup>50</sup> All of the evaluated nonlinear coefficients are summarized in Table 2. Nonlinear coefficient values such as the 2PA coefficient ( $\alpha_2$ ), nonlinear refractive index ( $n_2$ ) and saturation intensity ( $I_{\rm S}$ ) for the diverse glass compositions embedded with and without MNPs are enlisted in Table 3.<sup>51–57</sup>

Fig. 5(a) depicts the variation in the 2PA coefficient of the obtained glass samples as a function of different excitation wavelengths, while the inset depicts the variation of  $n_2$  with respect to the excitation wavelength. From Fig. 5(a), it was clear that the 2PA coefficient of the gold NP-embedded glasses followed a decreasing trend as the excitation wavelength moved away from the SPR region. This was attributed to the fact that the excitation wavelength closer to the SPR region of the Au NPs had a greater contribution on the optical nonlinearity than the one far away from the SPR region. Therefore, the nonlinear coefficient obtained at 700 nm was greater compared to that retrieved at 1000 nm. The possible errors mentioned in the table were due to the fluctuations in the laser power, the calculation of beam waist at Z = 0 and fitting procedures.

To address whether only 2PA or any other absorption processes contributed to the observed nonlinearity, intensitydependent NLO measurements were further performed on the SNBE and SNBEA-2 glass samples at 700, 800 and 900 nm excitations. The variation in the 2PA coefficients corresponding to the varied input intensities are depicted in Fig. 5(b). From this figure, it was evident that within the experimental errors, the variation in 2PA was more or less constant, which suggested that the mechanism involved in the observed nonlinearity was only from a 2PA process and the absence of other types of nonlinearities. Since the pulse duration used was very short ( $\sim$ 150 fs), the

**Table 2** Summary of NLO coefficients such as  $\alpha_2$  (2PA),  $I_S$  (saturation intensity),  $n_2$  (nonlinear refractive index) and the nonlinear susceptibility estimated from the *Z*-scan experiments of the Eu<sup>3+</sup> doped SNBE glasses embedded with and without Au NPs under an ultra-fast (150 fs) regime

Glass code	λ (nm)	$\alpha_2~(\times 10^{-11}~m~W^{-1})$	$I_{\rm S} (\times 10^{10} \text{ W m}^{-2})$	$n_2 (\times 10^{-18} \text{ m}^2 \text{ W}^{-1})$	$\operatorname{Re}\chi^{(3)}(\times 10^{-13} \text{ esu})$	$Im\chi^{(3)}(\times 10^{-13}~esu)$	$\chi^{(3)}$ (×10 <sup>-13</sup> esu)
SNBE	700	$0.19(\pm 0.02)$	_	$0.23 (\pm 0.03)$	1.53	0.71	1.68
	800	$0.14(\pm 0.01)$	_	$0.21(\pm 0.03)$	1.41	0.59	1.53
	900	$0.11(\pm 0.01)$	_	$0.21(\pm 0.03)$	1.41	0.53	1.51
	1000	$0.08(\pm 0.01)$	_	$0.20(\pm 0.03)$	1.33	0.42	1.39
SNBEA-1	700	$0.47(\pm 0.04)$	_	$1.04(\pm 0.15)$	6.98	1.76	7.19
	800	$0.36(\pm 0.04)$	_	$0.82(\pm 0.12)$	5.51	1.54	5.72
	900	$0.32(\pm 0.03)$	_	$0.71(\pm 0.10)$	4.77	1.45	4.99
	1000	$0.24(\pm 0.02)$	_	$0.62(\pm 0.10)$	4.16	1.28	4.35
SNBEA-2	700	$0.77(\pm 0.08)$	_	$1.22(\pm 0.18)$	8.30	2.92	8.79
	800	$0.61(\pm 0.06)$	_	$1.03(\pm 0.15)$	7.01	2.64	7.49
	900	$0.52(\pm 0.05)$	_	$0.74(\pm 0.11)$	4.56	2.53	5.21
	1000	$0.44(\pm 0.04)$	_	0.66 (±0.09)	3.95	2.38	4.61
SNBEA-3	700	0.06	$6.74 (\pm 0.67)$	$1.53(\pm 0.22)$	10.46	0.23	10.46
	800	0.03	$6.14(\pm 0.61)$	$1.19(\pm 0.17)$	8.14	0.13	8.14
	900	0.02	$6.02(\pm 0.60)$	$1.02(\pm 0.15)$	6.97	0.09	6.97
	1000	0.02	$5.63 (\pm 0.56)$	$0.81 (\pm 0.12)$	5.53	0.10	5.53

Table 3 NLO coefficients of select glass compositions

Glass composition	Wavelength and pulse sizes	$\alpha_2 (\times 10^{-11} \text{ m W}^{-1})$	$I_{\rm S} ({\rm W} {\rm m}^{-2})$	$n_2 (m^2 W^{-1})$	Ref.
$45Bi_{2}O_{2}-30ZnO-25B_{2}O_{2}$	800 nm (110 fs)	1.04	_	$1.5 \times 10^{-19}$	51
2-32-3	532  nm (30  ps)	24.6		_	51
Fused silica	1064 nm	_	_	$2.7 imes10^{-20}$	52
	355 nm	$1.25 imes10^{-3}$	_	$2.5 imes10^{-20}$	52
BK-10 (borosilicate crown glass)	1064 nm	_	_	$2.8 \times 10^{-20}$	52
	355 nm	0.0055	_	$1.7 imes 10^{-20}$	52
9.9Na <sub>2</sub> O-10ZnO-80B <sub>2</sub> O <sub>3</sub> -0.1AuCl <sub>3</sub>	800 nm (150 fs)	$5.2 imes10^{-3}$	$1.4 imes10^{11}$	$-1.2\times10^{-16}$	53
29.9Na <sub>2</sub> O-10ZnO-60B <sub>2</sub> O <sub>3</sub> -0.1AuCl <sub>3</sub>	800 nm (150 fs)	$8.1 imes 10^{-3}$	$6.5 imes10^{11}$	$-2.8\times10^{-16}$	53
33SiO <sub>2</sub> -9.5Al <sub>2</sub> O <sub>3</sub> -32.5CdF <sub>2</sub> -19.5PbF <sub>2</sub> -5.5ZnF-	480 nm (8 ns)	150	$7 imes 10^{10}$	_	54
small amount of AgNO <sub>3</sub>					
5Na <sub>2</sub> O-20B <sub>2</sub> O3-75SiO <sub>2</sub> -2Cu(NO <sub>3</sub> ) <sub>3</sub> (wt%)	800 nm (190 fs)	$4.1 imes 10^{-2}$	—	$5.3 \times 10^{-20}$	55
5.74Na <sub>2</sub> O-21.38B <sub>2</sub> O <sub>3</sub> -72.88SiO <sub>2</sub> -1.25Cu(NO <sub>3</sub> ) <sub>3</sub>	800 nm (150 fs)	2.1	—	$6.42\times10^{-17}$	56
58.4GeO <sub>2</sub> -41.6Bi <sub>2</sub> O <sub>3</sub> -3Au <sub>2</sub> O <sub>3</sub> -0.5Eu <sub>2</sub> O <sub>3</sub> (wt%)	540 nm (120 fs)	—	$0.11  imes 10^{11}$	$1.8 imes10^{-19}$	57



**Fig. 5** (a) Variation in the two-photon absorption coefficient ( $\alpha_2$ ) as a function of the excitation wavelength. The inset shows the variation in the nonlinear refractive index ( $n_2$ ) with respect to the excitation wavelength. (b) Variation in the two-photon absorption coefficient ( $\alpha_2$ ) as a function of the incident laser fluence.

possibility of an excited-state absorption was neglected. However, the high repetition rate ( $\sim$  80 MHz) could have resulted in thermal nonlinearities.

To identify the influence of the Eu<sup>3+</sup> ion on the non-linear coefficients, the nonlinear absorption and refraction coefficients of

the Eu-free glass (*i.e.*,  $55b_2O_3$ - $25Na_2O$ - $70B_2O_3$ ) was measured at 800 nm and the values were identified as  $0.075 \times 10^{-11}$  m W<sup>-1</sup> and  $0.153 \times 10^{-18}$  m<sup>2</sup> W<sup>-1</sup>, respectively. Therefore the strong nonlinear coefficients of the SNBE glass (Table 2) were attributed to the hyperpolarizability of the Eu<sup>3+</sup> ions.<sup>58</sup> From the linear optical absorption, the characteristic absorption peak of the Eu<sup>3+</sup> ion was not observed in the near IR region. Therefore, resonant effects were ruled out. It was reported that the third order optical nonlinearity was ascribed to the hyperpolarizability of the glass components and the dipole moment of the corresponding ions according to the expression,<sup>58</sup>

$$p(t) = \alpha^{(1)} E_{\rm loc}(t) + \frac{\alpha^{(3)}}{6} (E_{\rm loc}(t))^3$$
(7)

where *p* is the stimulated dipole moment of the ion,  $\alpha^{(1)}$  is the ion's polarizability,  $\alpha^{(3)}$  is the hyperpolarizability of the ions,  $E_{\rm loc}$  is the local field of the ions and *t* is the time component. In the glasses, the third order nonlinear optical susceptibility,  $\chi^{(3)}$  was strongly associated with the local electric field ( $E_{\rm loc}$ ) and hyperpolarizability ( $\alpha^{(3)}$ ) according to the following equation:<sup>58</sup>

$$\chi^{(3)}(-\omega;\omega_1,\omega_2,\omega_3) = \frac{L(\omega)L(\omega_1)L(\omega_2)L(\omega_3)}{24} \sum_i N_i \alpha_i^{(3)} \quad (8)$$

where the subscript '*T* is the contribution from the constituent '*i*',  $N_i$  is the number density of '*i*' and  $L(\omega)$  is associated with the local electric field for an isotropic medium such as glass  $\omega = \omega_1 = \omega_2 = \omega_3$ . Furthermore, the local field enhancement factor ( $\eta$ ) for the NPs of diameter '*D*' embedded in the glasses and separated by the distance '*d*' is given by,<sup>31</sup>

$$\eta = E_{\rm loc}/E_i = (D+d)/d \tag{9}$$

From the TEM measurements and Mie theory calculations, it was clear that the particle size of the Au NPs increased with the increase in the doping level of AuCl<sub>3</sub>. Furthermore, the inter particle distance decreased as a function of the AuCl<sub>3</sub> content. Therefore, the local field enhancement factor increased with the increase in the particle size and decreased in the inter-particle distance of the Au NPs.

From eqn (8), it was clear that the nonlinear susceptibility was directly related to the local field and hyperpolarizability. The magnitudes of the estimated polarizability of all the glass

samples used in the study (tabulated in Table 1) clearly indicated an enhancement in the optical nonlinearity with respect to the gold content. This might have been due to the hyperpolarizability of the non-bridging lone electron pairs<sup>59</sup> of the Eu<sup>3+</sup> ions stimulated by the local field effect. These non-bonded 4f<sup>6</sup> electrons of the Eu<sup>3+</sup> ions were effectively screened from the nucleus due to the local field stimulation by the SPR of the Au NPs, which permitted large charge displacements and improvised the third order nonlinear susceptibility.<sup>59</sup> Since there were no absorption peaks for Eu<sup>3+</sup> and the Au NPs in the region of the excitation wavelengths, the mutual transfer of energy from the Eu<sup>3+</sup> ions to the Au NPs and vice versa were ruled out and the resonant effects were also ignored. We concluded that the enhancement in the optical nonlinearity in the Au NP-embedded glasses can be ascribed to the local filed stimulated by the SPR of the gold NPs. It was reported that in the state of weak confinement, the NLO property was enhanced until the excited state was coherent, while the particle size increased to a certain definite value because of the size-dependent exciton oscillator strength.<sup>60</sup> After this threshold particle size, the growth of the particle size resulted in a deviation from the ideal harmonic oscillator<sup>60</sup> model, causing the SA nonlinearity observed in the SNBEA-3 glass.

The switching of the nonlinear absorption from RSA to SA as the AuCl<sub>3</sub> content increased in the glass composition could also be explained as follows. Normally, the NLO response of the glasses embedded with MNPs mainly originated from the localfield effects induced by the SPR of the MNPs.<sup>61</sup> When the size of the NPs was smaller, the displacement of the charges was homogeneous and yielded a dipolar charge distribution, which induced a local electric field to enhance the third-order nonlinearity. However, when the size of the NPs increased, the displacement of the electronic cloud was not homogenous for the spherical NPs. Therefore, higher order multipolar charge distributions were induced, resulting in the SA as observed in the SNBEA-3 glass.<sup>61</sup> From earlier studies, it was also concluded that the local-field enhancement factor strongly depended on the particle size and composition of the substrate.<sup>62</sup> In our case, with the increase in the AuCl<sub>3</sub> concentrations, the results of the OA Z-scan measurements changed for the larger sized Au NPs. When the samples were irradiated by a laser during the Z-scan measurements, the electron clouds of the Au NPs induced a local electrical field, which possibly became a dominant factor in enhancing the third-order nonlinearity. However, the interactions between the substrate and the NPs themselves became stronger with the increase in the size of the NPs. In such a case, the local electrical field induced by the NPs was not the dominant factor on its optical nonlinearity. The interaction of the NPs weakened the local electrical field and the electron clouds distortion of the network structure, which was also induced by laser irradiation. Consequently, this could possibly have resulted in an adverse change in the nonlinear absorption. We believe that there was a threshold size for the Au NPs to make the NPs contribute mostly to a third-order optical nonlinearity. However, to understand this threshold size (and other effects), more investigations are needed (the nonlinearity for a large number of samples needs to be measured)

to identify the exact reason for the observed large nonlinearity, which will be a part of our future investigations.

The glasses that possess a high 2PA and low  $n_2$  are very effective for NLO device applications (e.g., optical limiters). Therefore, the figure of merit (FOM) is one proposed parameter for the materials or glasses in practical NLO device applications. Glasses can be used for fabricating optical switches if the FOM < 1. Whereas, if the FOM > 1, the glasses are beneficial for manufacturing optical limiters.<sup>50</sup> The FOM of all the studied glass samples at each excitation wavelength was determined.<sup>53</sup> It was found that the examined glass samples possessed FOM > 1 at all the excitations. Hence, the studied glasses were competing materials for the fabrication of the optical limiters at the studied wavelength regions. However, the glasses containing a higher concentration of gold (0.02 mol%, SNBEA-3) demonstrated a SA in the OA Z-scan and a FOM < 1. Therefore, the SNBEA-3 glass was not suitable for use in the optical limiters in the studied region. However, the materials with SA have the potential for mode-locking applications involving ultra-fast lasers.

#### 3.3. Photoluminescence properties

The PL excitation spectra of the Eu<sup>3+</sup> emission at 613 nm  $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$  for the SNBE and SNBEA [Fig. 6(a)] glasses exhibited excitation peaks within 350 to 400 nm, which were observed from inherent transitions that originated from the  ${}^{7}F_{0}$  and  ${}^{7}F_{1}$ ground states to different Eu<sup>3+</sup> excited states<sup>63</sup> as labeled in Fig. 6(a). In all of the studied glasses, the sharp excitation line at 393 nm (Eu<sup>3+</sup>:  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ ) showed the highest intensity. The emission spectra of Eu<sup>3+</sup> (0.5 mol%) containing the SNBE and SNBEA glasses recorded at the excitation of 393 nm [Fig. 6(b)] was mainly composed of Eu<sup>3+</sup> characteristic emission lines positioned at 578, 592, 613, 652, 703 and 746 nm, which were attributed to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  (J = 0-5) transitions of the Eu<sup>3+</sup> ions.36 The strongest luminescence line positioned at 613 nm (red:  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ) was hypersensitive and allowed for the electric dipole (ED) transition. It was also strongly responsive to the site occupation of the Eu<sup>3+</sup> ions for inversion or anti-inversion symmetry,<sup>64</sup> while the second strongest PL line positioned at 703 nm was the ED  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition.<sup>24</sup> The less PL intense line at 578 nm was originally a forbidden  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition because of the same J = 0 value.<sup>63</sup> The PL line positioned at 592 nm (orange) was a magnetic dipole (MD) that allowed for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition and was not very responsive to the variation in the crystal field environment of the host matrix. The PL peak at 652 nm was a mixed MD and ED  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transition.<sup>24</sup> To quantify the contribution of the MNPs on the PL enhancement of the Eu<sup>3+</sup> ions, a luminescence enhancement factor (LEF) was used. The LEF is the ratio of PL peak intensity of the Eu3+-containing glasses embedded with MNPs to the Eu<sup>3+</sup>-containing glasses without MNPs. The LEF of the SNBEA-1, 2 and 3 glasses for the 613 nm PL peaks were 2.98, 3.58 and 1.2, respectively. For the 703 nm peak, the LEF values were 13.36, 11.94 and 8.49, respectively, for the SNBEA-1, 2 and 3 glasses. The LEF values of all the gold NP-embedded glasses for each PL Eu<sup>3+</sup> peak are enlisted in Table 4. Fig. 6(b) indicates that in the glasses



**Fig. 6** (a) Room temperature excitation spectra ( $\lambda_{emi} = 613$ ). (b) Photoluminescence spectra ( $\lambda_{exc} = 393$  nm) of Eu<sup>3+</sup> containing alkali borate glasses embedded with different concentrations of the Au NPs. The PL optical image of the Eu<sup>3+</sup> containing glass embedded with 0.01 mol% AuCl<sub>3</sub> is also shown in figure (b).

without the Au NPs, the PL intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition positioned at 592 nm was comparable in magnitude to that of the PL intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition positioned at 703 nm. Nonetheless, after the addition of AuCl<sub>3</sub> to the glass system, the PL intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition for Eu<sup>3+</sup> increased significantly. The glass system had a positive effect on the PL of the Eu<sup>3+</sup> transitions at 613 and 703 nm peaks after the addition of AuCl<sub>3</sub> to the glass composition. The inset of Fig. 6(b) shows that the red color intensity of the Eu<sup>3+</sup>-containing glass routed with the gold NPs (SNBEA-2 glass) was even visible for naked eyes. The enhancement in the Eu<sup>3+</sup> emission intensity with the incorporation of the Au NPs [Fig. 6(b)] was possibly either because of the local field effect (LFE) near the Eu<sup>3+</sup> ions persuaded by the gold NPs and/or due to the energy transfer among the Au NPs to the Eu<sup>3+</sup> ions.<sup>2,65</sup> The highest improvement in the PL intensity was observed for 0.01 mol% gold, above which, quenching in the PL intensity was observed. From Table 1, it was identified that with the increase in the doping level of the AuCl<sub>3</sub> concentration, the average Au-Au distance  $(d_{Au-Au})$  decreased and hence enhanced the local field. Therefore, the LFE stimulated by the gold NPs near the Eu<sup>3+</sup> ions was responsible for the luminescence enhancement. It is known that the relative permittivities (dielectric) of the glass host and the MNPs are different from each other. In addition, surface plasmon polaritons are caused by the oscillations of

Table 4 The luminescence enhancement factor (LEF) values of the emission transitions for the investigated  $Eu^{3+}$ :Au co-doped glasses

Transition	SNBE	SNBEA-1	SNBEA-2	SNBEA-3
$\overline{{}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{0}}$	1	1.54	1.95	0.66
${}^{5}\mathrm{D_{0}} \rightarrow {}^{7}\mathrm{F_{1}}$	1	1.74	2.13	0.83
${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	1	2.98	3.58	1.2
${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	1	6.36	8.65	3.85
${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{4}$	1	11.36	11.94	8.49

electrons moving along the surface of MNPs and the focus of light in the subwavelength structures.<sup>65</sup> The secondary reason for the enhanced PL was that when  $Eu^{3+}$  was present in close vicinity to the metal surface, weak PL emissions from the Au NPs were added as a second channel of excitation energy, that is, the energy transfer (ET) from the Au<sup>0</sup> to  $Eu^{3+}$  ions.<sup>66</sup> Thus, as the Au NPs increased the photonic density around the  $Eu^{3+}$  ions situated in the near vicinity, there was an increase in the number of photons captured by the  $Eu^{3+}$  ions. As a result of the superior excitation rate, the population of the excited state of the  $Eu^{3+}$  ions increased. However, the transfer of energy from the Au<sup>0</sup> NPs to the  $Eu^{3+}$  ions was expected to play a minor role because the excitation wavelength did not overlap with the SPR absorption of the Au NPs (excitation wavelength was slightly far away from the SPR absorption of the Au NPs).

Reportedly,<sup>2</sup> when the size of the MNPs is less than the incident light ( $d \ll \lambda_{exc}$ ), the interaction of light with the MNPs cause the oscillation of the electrons in the conduction band. A concentrated electromagnetic field was stimulated by these oscillations, thus contributing to the improvement in the local electric field around the NPs.<sup>2</sup> Eventually, the electric field near the RE ions located in the proximity of the MNPs increased. This enhanced the excitation and emission rates of the Eu<sup>3+</sup> ions effectively, and thereby the intensity of the Eu<sup>3+</sup> PL lines increased. Another possible reason for the PL improvement was the coupling of the Eu<sup>3+ 5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> transition dipoles with resonant plasmon modes in the gold NPs.<sup>67</sup> As demonstrated from the TEM results, with an increase in the AuCl<sub>3</sub> concentration, the growth of the Au NPs occurred by the Ostwald's ripening process. This resulted in a decreased average Au-Au  $(d_{Au-Au})$  and Au-Eu  $(d_{Au-Eu})$  distance. In reality, during the growth process of the gold NPs, the Eu<sup>3+</sup> ions might have entered the Au NPs phase, resulting in a strong electromagnetic field around the Eu<sup>3+</sup> ions and diminished PL peak intensities for Eu<sup>3+</sup>. Thus, the PL intensity for the quenching of Eu<sup>3+</sup> was attributed to the energy transfer (ET) from the excited Eu<sup>3+</sup> ions to the Au NPs.<sup>68</sup> In other words, the separation between the RE ion and the MNPs (or metallic aggregate) became smaller, which contributed to increased multipole interactions that favoured the energy transfer from the RE ions to the gold NPs. In addition, this resulted in optical re-absorption by non-plasmonic molecules like Au particles (ML-Au), which was in resonance with the emissions from the Eu<sup>3+</sup> ions.<sup>68</sup> Therefore, the dipole-dipole interaction between them may have contributed to the energy transfer from the Eu<sup>3+</sup> ion to the Au NPs. Therefore, the PL intensity was quenched in the SNBEA-3 glass as evidenced in Fig. 6(b). Similar observations

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were also reported recently by Yu et al.<sup>16</sup> in tellurite glasses doped with Au NPs and by Saad et al.<sup>2</sup> in phosphate glasses doped with Ag NPs. The absorption spectra did not demonstrate any additional absorption bands for the various ionic species, except for the characteristic absorption peaks of the Eu<sup>3+</sup> ions and the SPR band of the Au<sup>0</sup> NPs. Nonetheless, the excitation spectrum obtained by monitoring the standard PL peak positioned at 613 nm resulted in the excitation bands of the Eu<sup>3+</sup> ions since the concentration of the thermal reducing agent  $(Sb_2O_3)$  used in the composition was high (5 mol%) in contrast to the AuCl<sub>3</sub> concentration (0.005-0.02 mol% Au). Therefore, the co-existence of various ionic species that served as optical centers was ruled out. Nevertheless, since the emission transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  of Eu<sup>3+</sup> was never broken by a crystal field, the occurrence of a single peak at 578 nm was used as proof that only a single Eu<sup>3+</sup> ion was responsible for the series of emission transitions depicted in the emission spectra.<sup>69</sup>

The enhancement in the PL intensity of the Eu<sup>3+</sup> ions at the initial doping of AuCl<sub>3</sub> and the decrease in the intensity at higher concentrations was explained as follows. With the increasing concentration of Au from 0.005 mol% to 0.01 mol%, both the size and number of Au NPs increased. The strong local electric field in the Au NPs increased from the SPR excitations, which led to the enhancement of the electric fields from the exciting and emitting photons by the excited NPs as well as the improvement in the PL intensity.<sup>70</sup> However, the PL intensity could not increase continuously with the increasing size of the NPs. Beyond a certain concentration of Au NPs, the PL intensity gradually decreased. When the size of the NPs was too small compared to the mean free path of the conduction electrons inside the particles, the collision of the conduction electrons with the surface of the NPs caused damping of the SPR excitations and PL intensity remained low. With an increasing concentration, the particle size increased and consequently, the damping effect decreased. As a consequence, the PL intensity increased gradually until the size of the NPs was lower than the value of the mean free path. When the size of the NPs exceeded the value of the mean free path, a decrease in the PL intensity was observed due to the radiative damping effect.71,72

The MD transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  was not relative to the glass host and the other ED allowed for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  (*J* = 2, 4 and 6)

transitions, which greatly depended on the structure and site of asymmetry around the Eu<sup>3+</sup> ion.<sup>64</sup> The goodness of the glass host for the red lasing action was represented via the intensity ratio (*R*) between  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ . The *R*-value gave insight into the symmetry of the ligand field and the covalency of the metal-ligand bond.<sup>3</sup> The R-values for SNBE, SNEA-1, 2 and 3 were 4.37, 5.67, 5.77 and 5.26, respectively (Table 5). The *R*-values were greater than the unity for all of the studied glasses, which suggested that the Eu<sup>3+</sup> ions were situated in acentric crystalline sites.<sup>64</sup> Moreover, the R values of the studied glasses were found to increase from 3.37 to 5.77 upon incorporating the Au NPs for the glass host. Then, it decreased in the SNBEA-3 glass. The interplay between the sharply spaced Au NPs representing the coupled SPR and the increase in the Au NP concentration was expected to result in a distortion of the crystal field.<sup>73</sup> However, the decrease in the asymmetric ratio observed in the SNBEA-3 sample was an indication that the crystals or NPs were a more regularly oriented dispersion of the gold NPs, thus resulting in a clearly resolved stark splitting of the emission bands due to the crystal field effect. This finding clearly indicated that the interaction between the Eu<sup>3+</sup> ions and the Au NPs strongly influenced the crystal field environment of the RE ions. The higher value of R corresponding to 5.77 for the SNBEA-2 glass demonstrated the potential use of the investigated glass as a laser host material. The R values were comparably larger than the reported values for the Eu<sup>3+</sup> doped glasses as evidenced by Table 5.

The Au concentration mediated the quantum efficiencies of the present glasses, which were also measured with a CCE spectrophotometer (BRC112E) attached with a specially designed integrating sphere using a method mentioned elsewhere.<sup>74</sup> The quantum efficiency of the SNBE sample was obtained as 17.2% and it was elevated to 51.47% and 62% with the increase in the Au concentration for the SNBEA-1 and SNBEA-2 samples. As mentioned previously, the reduction in the average Au–Au distance with the increase in the doping level of the AuCl<sub>3</sub> concentration promoted the local field. Therefore, the LFE that was stimulated by the gold NPs near the Eu<sup>3+</sup> ions was responsible for the enhancement. The further increase in the Au concentration in SNBEA-3 led to a reduction in the quantum efficiency to 20.26%.

Table 5	Judd-Ofel	t parameters (	( $arOmega_{\lambda}, imes10^{-20}$	cm <sup>2</sup> ) of the	<sup>5</sup> D <sub>0</sub> level o	of the Eu <sup>3+</sup>	doped g	glasses along	with the	e intensity	ratio (R)	values fo	or the studie	ed
glasses v	vith select g	lass compositi	ions											

Glass codes/composition	$\Omega_2$	$\Omega_4$	$\Omega_6$	Intensity ratio (R)	Ref.
SNBE	2.24	1.151	0	3.37	Present work
SNBEA-1	8.49	0.160	0	5.67	Present work
SNBEA-2	9.60	0.254	0	5.77	Present work
SNBEA-3	7.81	0.119	0	5.26	Present work
44.5P <sub>2</sub> O <sub>5</sub> -44.5Na <sub>2</sub> O-10ZnO-1Eu <sub>2</sub> O <sub>3</sub>	_	_	_	2.42	2
44.25P2O5-44.25Na2O-10ZnO-1Eu2O3-0.5AgNO3	2.91	0.15	_	2.51	2
44.25P <sub>2</sub> O <sub>5</sub> -44.25Na <sub>2</sub> O-10ZnO-1Eu <sub>2</sub> O <sub>3</sub> -0.5AgNO <sub>3</sub> heat treated at 305 °C for 20 h	3.35	0.27	_	2.55	2
44.25P <sub>2</sub> O <sub>5</sub> -44.25Na <sub>2</sub> O-10ZnO-1Eu <sub>2</sub> O <sub>3</sub> -0.5AgNO <sub>3</sub> heat treated at 305 °C for 30 h	3.18	0.19	_	2.13	2
54.9B <sub>2</sub> O <sub>3</sub> -9P <sub>2</sub> O <sub>5</sub> -15BaO-15ZnO-5Al <sub>2</sub> O <sub>3</sub> -1Eu <sub>2</sub> O <sub>3</sub> -0.1AgNO <sub>3</sub>	2.15	0.33	0	2.49	3
54B <sub>2</sub> O <sub>3</sub> -9P <sub>2</sub> O <sub>5</sub> -15BaO-15ZnO-5Al <sub>2</sub> O <sub>3</sub> -1Eu <sub>2</sub> O <sub>3</sub> -1AgNO <sub>3</sub>	4.27	0.59	0	2.96	3
Silicate glasses	9.65	6.68	—	—	78
Alkali tellurite glasses	11.06	4.58	—	—	79

The Judd–Ofelt<sup>75,76</sup> (JO) parameters  $\Omega_{\lambda}$  ( $\lambda$  = 2, 4, 6) provided information about the structural changes occurring in the samples when the MNPs were incorporated. Because of this, the JO attributes were calculated using emission spectra and are tabulated in Table 5. Among the three JO parameters,  $\Omega_2$  is associated with the short-range effects viz., polarizability of the ligand ions, covalency of Eu<sup>3+</sup>-O bonds and the asymmetry of the ligand environment around the Eu<sup>3+</sup> ion site. The  $\Omega_A$  and  $\Omega_G$ attributes represent the long-range effects viz., viscosity and the rigidity of the glass. In the present investigation, the value of  $\Omega_6$ was considered to be zero since the corresponding squared reduced matrix element was zero. Also, a transition from  ${}^{5}D_{0} \rightarrow {}^{7}F_{6}$  was not observed in the emission spectra of the presently studied glass samples, which prevented the estimation of the  $\Omega_6$  JO parameter.<sup>3</sup> Nonetheless, the higher value of  $\Omega_2$  in the studied glasses indicated a higher local asymmetry around the Eu<sup>3+</sup> ions.<sup>77</sup> From the Table 5 data, it was observed that the  $\Omega_2$  parameter increased as a function of the gold concentration up to 0.01 mol% and then decreased at higher concentrations. This increasing trend of  $\Omega_2$  represented the enhancement in the covalency of the metal-ligand bond in the investigated glasses and the decrease in the symmetry of the ligand environment around the Eu<sup>3+</sup> ions. In addition, the increase in  $\Omega_2$  in the present investigation was interpreted as the increase in the Au NP concentration increasing the number of Eu<sup>3+</sup> ions in the glass network that occupied asymmetric and more polarized sites. The JO parameters of some recently reported glasses are tabulated in Table 5. It was found that the  $\Omega_2$  value of the glasses studied in the present investigation was larger than those of the silver NP-embedded, Eu<sup>3+</sup>doped, phosphate glasses<sup>2</sup> and the Eu<sup>3+</sup>-doped boro-phosphate glasses embedded with silver NPs.3 Furthermore, the values were comparable with those of silicate glasses.<sup>78</sup> This indicated that the Eu<sup>3+</sup> ions in the prepared glasses presented a higher covalency for the ion-ligand and a lower symmetry compared with the phosphate, boro-phosphate and silicate glasses. This strongly suggested that the SNBEA-2 (borate) glass was a potentially active host for the emission of red light and practically appropriate for the design of display devices compared to other glass families. On the other hand, the reported values were lower than those of alkali tellurite glasses.79

The speciality or unusualness of the emission spectra depicted in Fig. 6(b) is the minimal PL intensity of the  ${}^5D_0 \rightarrow {}^7F_0$  transition and the anomalous strong PL intensity of the  ${}^5D_0 \rightarrow {}^7F_4$  transition after the  ${}^5D_0 \rightarrow {}^7F_2$  transition. In literature, usually the enhancement in the intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  transition of Eu<sup>3+</sup> is observed with respect to the glass composition, the RE ion concentration and the MNP concentration along with the temperature treatment.<sup>2,3,23-25</sup> The intensity enhancement of the  ${}^5D_0 \rightarrow {}^7F_4$  transition did not provide an explanation for most investigations of the Eu<sup>3+</sup>-containing glasses because the features were too weak.<sup>2,3,16,24</sup> In the present investigation we observed an abnormal intensity enhancement when the gold NPs were embedded in the glass composition, which might have been linked with the nonlinear intensity enhancement of the  ${}^5D_0 \rightarrow {}^7F_4$  transition. The anomalous enhancement in the intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition of Eu<sup>3+</sup> could be explained as follows. The JO parameters,  $\Omega_{\lambda}$ , are hypothetically given by<sup>26,27</sup>

$$\Omega_{\lambda} = (2\lambda + 1) \sum_{l,p} \frac{|B_{\lambda lp}|^2}{(2l+1)}$$
(10)

In the above equation,  $B_{\lambda tp}$  is given by

$$B_{\lambda tp} = \frac{2}{\Delta E} \langle r^{t+1} \rangle \theta(t,\lambda) \gamma_p^t - \left[ \frac{(\lambda+1)(2\lambda+3)}{(2\lambda+1)} \right]^{1/2} \\ \times \langle r^{\lambda} \rangle (1-\sigma_{\lambda}) \langle f \| C^{(\lambda)} \| f \rangle \Gamma_p^t \delta_{t,\lambda+1}$$
(11)

where,  $\Delta E$  is the energy difference between the barycenters of the excited  $4f^{N-1}5d$  and ground  $4f^N$  configurations,  $\langle r^x \rangle$ is a radial expectation value,  $\theta(t, \lambda)$  is a numerical factor,  $(1 - \sigma_{\lambda})$  is a shielding factor,  $\langle f \| C^{(\lambda)} \| f \rangle$  is one-electron reduced matrix element and  $\delta_{t,\lambda+1}$  is the Kronecker delta function. On the right side of eqn (11), the first term represents the contribution of the static forced electric dipole mechanism and the second term corresponds to the contribution of the ligand polarizability-dependent dynamic coupling mechanism.<sup>28</sup> The term  $\gamma_p^t$  is a so-called odd-rank, ligand field parameter and  $\Gamma_p^t$  (t = 1, 3, 5, 7) contains the dependence on the coordination geometry as well as the nature of the chemical environment around the RE ion, which can be described by,<sup>28</sup>

$$\gamma_{p}^{t} = \left(\frac{4\pi}{2t+1}\right)^{1/2} e^{2} \sum_{j} \rho_{j} (2\beta_{j})^{t+1} \frac{g_{j}}{R_{j}^{t+1}} Y_{p}^{t} \left(\theta_{j}, \varphi_{j}\right)$$
(12)

$$\Gamma_p^t = \left(\frac{4\pi}{2t+1}\right)^{1/2} \sum_j \frac{\alpha_j}{R_j^{t+1}} Y_p^t \left(\theta_j, \varphi_j\right)$$
(13)

where in eqn (12),  $\rho_j$  is the magnitude of the total overlap between the 4f and ligand wave functions and  $\beta_j = 1/(1 + \rho_j)$ and  $g_j$  are the charge factors. Eqn (12) can be demonstrated as a ligand field parameter produced by the effective charges,  $\rho_j g_j e$ , located at the mid-points of the RE-ligand chemical bonds.<sup>26</sup> In eqn (13),  $\alpha_j$  is the isotropic polarizability of the *j*th ligand atom or a group of atoms at position  $R_j$  and  $Y_p^t$  is the spherical harmonic of the rank, *t*.

According to the electric dipole transition intensity calculation using JO theory, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is governed by the operator  $\Omega_{2}$ , whereas the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition is governed by  $\Omega_{4}$ . It was reported that if the RE ion is positioned at the inversion centre, then both  $\gamma_{p}^{t}$  and  $\Gamma_{p}^{t}$  vanish identically.<sup>27</sup> We considered a theoretical analysis in which we departed from a large symmetry with a center of inversion and kept distorting the chemical environment towards a lesser symmetry. The distortion allowed for the first  $\gamma_{p}^{t}$  and  $\Gamma_{p}^{t}$  to be of a greater rank (t = 5 and 7), which greatly influenced the  $\Omega_{4}$  and  $\Omega_{6}$  intensity parameters.<sup>27</sup> The lower odd-rank  $\gamma_{p}^{t}$  and  $\Gamma_{p}^{t}$  (t = 3, correspondingto  ${}^{5}D_{0} \rightarrow {}^{7}F_{2})$  were more sensitive to changes in symmetry<sup>28</sup> and the contribution of the dynamic coupling effects induced by the MNPs were greater for the higher rank  $\gamma_{p}^{t}$  and

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 $\Gamma_p^t$  (t = 5, corresponding to {}^5D\_0 \rightarrow {}^7F\_4).<sup>26,28</sup> This may have accounted for the variation in the  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_4$ transitions as depicted in Fig. 6(b). Yi et al.<sup>26</sup> roughly demonstrated that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transitions were determined by the odd-rank static electric field parameters of the Eu<sup>3+</sup> site according to the point charge model, whereas the latter was further affected by the polarizability of the chemical environment around Eu<sup>3+</sup> following the covalent bond model. Ye et al.<sup>28</sup> further theoretically explained the observed improvement in the intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition for Eu<sup>3+</sup> when the ion was near Mo(vi) and under a laser power of 20 W cm<sup>-2</sup>. The increased polarizability of the MoO<sub>6</sub> group due to the laser light was cited as the basis for the increment. Therefore, we calculated the polarizability magnitudes of all the studied glass samples and have furnished the results in Table 1. It was seen that the polarizability values increased as a function of the AuCl<sub>3</sub> concentration in the glass composition. Therefore, we concluded that the intensity enhancement in the abnormal  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transitions was attributed to the high polarizability of the glass induced by the Au NPs. This also coincided with previous works on Eu-containing diverse materials.<sup>26-28,80-82</sup> This investigation and explanation provides a new approach to tune the PL of Eu<sup>3+</sup> ions depending on the polarization effect, which could be applied in displays and optoelectronic devices. However, this is the first explanation for the enhancement in the intensity of the abnormal  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transitions in glasses. Therefore, further investigation is required to explore the mechanisms more precisely.

Similar investigations, i.e., the effect of the MNPs or heat treatment on the PL properties of Eu<sup>3+</sup>-doped diverse glasses, were performed by different researchers at different excitation wavelengths.<sup>24,83-85</sup> Dousti et al.<sup>83</sup> and Zhu et al.<sup>84</sup> reported that the emission of the Eu<sup>3+</sup>-doped glasses was suppressed in the presence of the Ag NPs due to an energy transfer from the Eu<sup>3+</sup> ions to the Ag NPs. On the other hand, Malta *et al.*<sup>85</sup> and Kassab et al.24 observed an enhancement in the emission of Eu<sup>3+</sup>-doped glasses containing the NPs. The enhancement was attributed to the enlarged local electric field in the RE-NP separation. Yu et al.<sup>16</sup> studied the influence of Ag or the Au NPs singly-existing or co-existing on the PL properties of tellurite glasses doped with Eu<sup>3+</sup> ions. They demonstrated that the increase in the radiative decay rate induced by the Au NPs contributed to the PL enhancement of the Eu<sup>3+</sup> ions in the tellurite glasses. They also explained that the PL enhancement of the Eu<sup>3+</sup>-doped Ag NPs containing tellurite glasses was attributed to the enhancement of the local field induced by the Ag NPs. They further elucidated that the increase in the radiative decay rate induced by the Au NPs and the enhanced excitation field induced by the Ag NPs co-contributed to the luminescence enhancement of Ag and the Au co-existing Eu<sup>3+</sup>-doped tellurite glasses. Nevertheless, none of these papers demonstrated the enhancement of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition of Eu<sup>3+</sup> as a function of the MNPs. Due to the abnormal emission of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition along with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, the investigated gold NP-embedded glasses showed a deep-red emission.

## 4. Conclusions

In summary, we prepared Eu<sup>3+</sup>-doped alkali borate glasses embedded with Au NPs. The optical absorption data of the Eu<sup>3+</sup>-doped glasses containing the Au NPs demonstrated characteristic Eu<sup>3+</sup> peaks along with an Au<sup>0</sup> NP SPR band. The SPR peak of the gold NPs shifted towards a longer wavelength as a function of the AuCl<sub>3</sub> concentration. This red-shift in the SPR band of the gold NPs as a function of AuCl<sub>3</sub> was ascribed to the growth of the Au NPs, which occurred due to the Ostwald's ripening process. The NLO measurements at near IR (700–1000 nm) for the singly doped  $Eu^{3+}$ co-embedded with the Au NPs established the optical limiting signatures, except at higher concnetrations of AuCl<sub>3</sub>. At higher concentrations (i.e., 0.02 mol%, sample SNBEA-3), the glass demonstrated a SA nonlinearity in the OA Z-scan mode. The enhancement in the optical nonlinearity in the Au NP-embedded glasses can be ascribed to the hyperpolarizability of the Eu<sup>3+</sup> ions for the glass-induced Au NPs. The NLO results and FOM estimation clearly proved that the studied glasses were beneficial for the fabrication of the optical limiters at the near IR regions. However, the glass containing a high concentration of the Au NPs was not suitable for limiting applications. The influence of the Au NPs on the PL properties of the Eu<sup>3+</sup> ions was studied in detail. It was observed that the PL intensity of the 613 nm emission peak for Eu<sup>3+</sup> was greatly enhanced by the incorporation of the gold NPs, which attributed to the local field effects. In addition to this 613 nm emission peak, the intensity of the 703 nm peak for the Eu<sup>3+</sup> ions was enhanced by embedding with the Au NPs. This was attributed to the improved polarizability of the glass caused by the Au NPs. However, at higher concentration of the gold NPs, the PL intensity decreased, which was due to a transfer of energy from  $Eu^{3+}$  to the Au NPs. The strong red luminescence under the UV excitation of the studied glasses revealed that the samples are appropriate for practical applications in many optoelectronic devices.

## Conflicts of interest

There are no conflicts to declare.

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