Contents lists available at ScienceDirect

Optical Materials

journal homepage: http://www.elsevier.com/locate/optmat

Effect of Eu^{3+} in tuning the ultrafast third-order optical nonlinearity in heavy metal borate glasses

P. Ramesh^{a,b}, Vinod Hegde^c, A.G. Pramod^a, B. Eraiah^a, S. Venugopal Rao^{d,***}, S. Shisina^{e,f}, Subrata Das^{e,f}, D.A. Agarkov^{g,h}, G.M. Eliseeva^g, G. Jagannath^{i,**}, M.K. Kokila^{a,*}

^a Department of Physics, Bangalore University, Bangalore, 560056, Karnataka, India

^b Govt. College for Women, Kolar, 563101, Karnataka, India

^c Department of Physics, Acharya Institute of Graduate Studies, Bangalore, 560107, India

^d Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad, 500046, Telangana, India

e Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram, 695019, Kerala, India

^f Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India

^g Institute of Solid State Physics RAS, 142432 Academician Osipyan str. 2, Chernogolovka, Moscow District, Russia

h Moscow Institute of Physics and Technology, 141700 Institutsky lane 9, Dolgoprudny, Moscow District, Russia

ⁱ Department of Physics, K S Institute of Technology, Bangalore, 560109, Karnataka, India

ARTICLE INFO

Keywords: Borate glasses Europium Heavy metal oxides Z-scan Polarizability Non-bridging oxygens

ABSTRACT

Photonic vitreous materials with high optical nonlinearities and fast response times are beneficial for designing next generation nonlinear photonic devices. Herein, large concentration of heavy metal oxide (PbO and Bi₂O₃) containing borate glasses activated with different Eu³⁺ concentrations have been designed through the melt quench technique. The non-linear optical (NLO) attributes such as nonlinear optical absorption and refractions were ascertained by utilizing the open aperture (OA) and closed aperture (CA) Z-scan techniques respectively in the spectral regions of 750–1000 nm using femtosecond laser pulses. The OA and CA Z-scan profiles demonstrated a reverse saturable absorption (RSA) nonlinearity (ascribed to two-photon absorption) and a positive nonlinear refraction nonlinearity (attributed to self-focusing effect) respectively. The NLO coefficients such as α_2 , n_2 and $\chi^{(3)}$ values were improved with respect to Eu³⁺ content in the glasses composition due to non-bridging oxygen and hyperpolarizability of Eu³⁺ ions. The NLO studies suggested that the examined glasses could be constructive materials for NLO device utilizations in the near infrared spectral regime.

1. Introduction

The recent advancements in communication technology created a growing need for the materials, which can be utilized to construct higher processing speed of switching element. In view of this, the materials with the high nonlinear optical (NLO) performance are essential to upgrade optical information technologies to next level. Basically, all optical switches engage the interaction among the photon and the medium to command the "turn on" and "turn off" of the optical signal transmission process at a fast rate (typically sub-picosecond or faster). It is utilized for all-optical signal regeneration, ultrafast wavelength conversion and optical limiting devices [1]. In the recent past, the researchers have mainly concerned about the fabrication of efficient optical switching devices and constantly searching for the relevant NLO materials with high nonlinear absorption and refraction coefficients to develop the materials for aforementioned applications [2,3]. Among the different materials of current interest, the glasses owing good third order optical nonlinearity due to absence of centrosymmetry are very much beneficial in NLO devices. Also, the third-order optical nonlinearity can be significantly tuned to meet specific requirement for a particular application by varying the glass compositions since the glasses are flexible in choosing the composition and can be prepared in desired shapes. In addition, the good mechanical stability and chemical resistivity of the glasses make them useful for several purposes [1]. Further, the glasses with high PbO and Bi₂O₃ content are believed to be promising materials for the utilization in the field of nonlinear optics

https://doi.org/10.1016/j.optmat.2020.110051

Received 29 March 2020; Received in revised form 25 April 2020; Accepted 22 May 2020 0925-3467/ $\[mathbb{C}\]$ 2020 Elsevier B.V. All rights reserved.



Invited Article



^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: soma_venu@uohyd.ac.in (S.V. Rao), jagannathgreddy@gmail.com (G. Jagannath), drmkkokila@gmail.com (M.K. Kokila).

because the Pb²⁺ and Bi³⁺ cations are main sources for high nonlinear refraction and absorption coefficients [4]. Further, it has been reported that third order nonlinear optical susceptibility $[\chi^{(3)}]$ of the glasses increases with the increase of heavy metal oxide (HMO) concentration in the glass composition. Therefore, it is required to design the glasses with high HMO content as high as possible. Nevertheless, the glass-forming region is considerably large for borate glass family than other conventional glass families. Hence, the borate glass is superior host for HMO since it vitrifies up to very high HMO content. Additionally, according to anionic group theory [5] the borate materials are of great interest because the nonlinear optical susceptibility $[\chi]$ mainly depends on the boron-oxygen anionic group and their coordination in the glass network. In corroborating to this, the improved NLO properties from borate materials have been obtained due to the presence of isolated $(BO_3)^{3-}$ groups [6]. Nonetheless, the borate glass structure majorly composed of isolated $(BO_3)^{3-}$ groups along with $(BO_4)^{5-}$, $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$, $(B_3O_9)^{9-}$ and $(B_4O_9)^{6-}$ groups etc. Hence, the improvement in nonlinear susceptibility in borate glasses can also be expected. Moreover, the optical threshold of borate glasses is high compared to other glasses, in view of this, it is important to take up the NLO investigation on borate glasses.

Furthermore, there are many reports on rare earth (RE) doped glasses for various photonic applications such as the development of new light sources, display devices, ultraviolet sensors and tuneable lasers and many more [7]. In spite of the scientific and technological interests on RE doped glasses, little interest has been given to their NLO properties. Surprisingly, the investigations related to the NLO properties of diverse glasses activated with RE ions are very few [7-12]. Recently, Santos et al. [7,13] and Nanda et al. [11] explained that, the NLO properties are enhanced significantly due to the polarizability of the RE ions. It has been also reported that the 4f electrons of RE ions are not involved in chemical bonding with network cations and they are effectively shielded from nucleus by external electric field and hence contribute to the hyperpolarizability, thereby improving the $\chi^{(3)}$ of the material significantly [14,15]. It is important to investigate the NLO properties at the spectral regions of commercially available lasers so that the practical utilization of materials is possible. In addition, for the practical functioning the material should possess the good optical nonlinearity at non-resonant spectral regions. In view of this Eu³⁺ ions are the good choice for doping since the Eu^{3+} ions are having very less absorptions cross section peaks at near infra-red (IR) region or absent in the glasses containing high concentration of HMOs thereby the resonant and/or energy transfer mechanisms can be ruled out.

Therefore, herein, the NLO properties of high HMO (PbO and Bi₂O₃) containing borate glasses activated with different concentration of Eu³⁺ are studied at near IR spectral regions using femtosecond (fs) laser pulses to evaluate their use in NLO devices and discussed the attenuations of nonlinear absorption and refraction as a function of excitation wavelength. The obtained NLO parameters are correlated with non-bridging oxygens (NBOs) and the polarizability of Eu³⁺ ions. Nevertheless, the Pb²⁺ and Bi³⁺ have similar electronic structure ([Xe] 4f⁴ 5 d¹⁰ 6s² 6p⁰) and their optical transition mechanisms resembles each other [12]. It is also quite interesting to compare the NLO properties of borate glasses containing these two HMOs.

2. Experimental details

Series of borate glasses activated with Eu_2O_3 were prepared through the melt-quenching method using porcelain (J-brand) crucibles based on the glass composition $10La_2O_3$ -50HMO-(40-*x*)B₂O₃-*x*Eu₂O₃ (with x =0, 0.5, 1 and 2 mol% and HMO = PbO, Bi₂O₃). The prepared samples were labelled as LPb50BEux and LBi50BEux for the lead and bismuthcontaining samples respectively, here *x* indicates the concentration of Eu₂O₃ in the glass composition. The starting reagents of high-grade oxides such as B₂O₃, PbO, La₂O₃ and Eu₂O₃ were procured from SD Fine Chemicals Ltd. for glass preparation and were used without

additional purification. The weighed 15 g of chemical composition was grinded thoroughly for homogenous. The well-mixed powder was transferred to porcelain crucible and kept for melting using muffle furnace. The lead-containing glass mixture was melted at 1050 °C and bismuth-containing glass mixture was melted at 1030 °C. After 20 min of melting, molten mass was quenched on pre-heated (200 °C) brass molds. The as-prepared glasses were annealed at 450 °C for 4 h to remove the thermal stress occurred while quenching from high temperature. Later, the annealed glass samples were highly polished using various grade emery sheets. The polished glasses were optically homogeneous to naked eyes and free from strains occurred due to synthesis conditions maintained. The glass transition (T_g) , onset crystallization (T_x) temperatures were evaluated using SDT Q 600 V8.3 build 101 Differential Thermal Analyzer (DTA) with a heating rate of 10 °C/min. Optical absorption spectra of all prepared glass samples were recorded utilizing PerkinElmer Lambda-35 UV-Visible spectrometer. The identification of structural groups formed in the glass network was carried out through Fourier transform infrared (FTIR) transmission measurement. Open aperture (OA) and closed aperture (CA) Z-scan measurements were executed for evaluating the nonlinear absorption and refraction properties of the prepared samples respectively in the spectral range of 750–1000 nm (insteps of 50 nm). The detailed experimental procedure of Z-scan technique has been summarized in our previous articles [16, 17].

3. Results

DTA profiles of Eu-free and corresponding 1 mol% Eu³⁺ doped LHMO50Eu1 (HMO = Pb, Bi) glasses are shown in Fig. 1. In general, the change between T_x and T_σ ($\Delta T = T_x - T_\sigma$) is referred as the estimation of glass forming ability or glass stability against crystallization [18]. To achieve a larger working range during operations for fiber drawing, we usually change the composition and the content of doping rare-earth and other factors to obtain a desirable ΔT . Since, the fibre drawing is a reheating process and ay crystallization during the process will strengthen the scattering loss of the fibre and worsen its optical properties. According to literature, if $\Delta T > 100$ °C, the glass system having relatively good thermal ability [18]. From DTA profiles, the T_g values of LPb50B, LBi50B, LPb50BEu1 and LBi50BEu1 glasses were found to be 468, 481, 468 and 464 $^{\circ}$ C respectively. Further, the T_x values of the respective glasses were found to be 603, 591, 587 and 577 °C. Furthermore, the ΔT values of the corresponding glasses were estimated to be 135, 110, 119 and 113 °C. All the examined glasses exhibited $\Delta T >$ 100 °C, indicating the examined glasses were more stable against devitrification and suited for fiber drawing. From the profiles, it can also be noticed that the thermal stability is decreased on incorporation of Eu^{3+} to the glass system evidenced by decrease in ΔT values as the Eu^{3+} added to the system.

The prepared glass samples exhibited a broad hump with absence of sharp crystalline peaks in the X-ray diffraction profiles as shown in Fig. 2 suggesting the glasses were amorphous in nature. The linear optical absorption spectra of LPb50BEux and LBi50BEux glasses are depicted in Fig. 3 (a) and (b), respectively. The glasses activated with 0.5 mol% of Eu³⁺ exhibit a single absorption due to $^{7}F_{0}\rightarrow^{5}D_{2}$ transition at 464 nm [19]. An additional absorption peak at 393 nm corresponding to $^{7}F_{0}\rightarrow^{5}L_{6}$ transition appeared in the lead-containing samples for higher Eu³⁺ concentration [19]. The absorption intensity of absorption peaks increased with Eu³⁺ content and highest for 2 mol% doped glasses. The several other absorption bands of Eu³⁺ ion in the UV and visible region not observed or masked in the present glasses due to strong absorption of the host glass [20]. The existence of heavy metal cations Pb²⁺ and Bi³⁺ respectively in LPb50BEux and LBi50BEux glasses might be the reason for the strong absorption of the glasses.

The FTIR spectra of Eu-free LPb50B and LBi50B glasses are shown in Fig. 4. Majorly there are three bands in the spectra which are in agreement with those mentioned in Refs. [21–23]. It has been largely



Fig. 1. DTA profiles of undoped and 1 mol % Eu^{3+} doped glasses.



Fig. 2. The XRD profiles of undoped and 1 mol% Eu^{3+} doped glasses.

accepted that the band around $1100-1500 \text{ cm}^{-1}$ is ascribed to stretching vibration of B–O bonds of trigonal $(BO_3)^{3-}$ groups in metaborate, pyroborate and orthoborates [21], whereas the band around 750–1100 cm⁻¹ is ascribed to stretching vibration of B–O bonds in tetrahedral $(BO_4)^-$ groups [24]. The transmission band at around 690–700 cm⁻¹ is due to the bending vibrations of the B–O linkages in the borate network [21]. The weak band at 621 cm⁻¹ observed in lead-containing glass can possibly be attributed to bending vibration of O–B–O bonds of borate

units [25]. Nevertheless, the IR analysis of the Bi₂O₃-containing glasses demonstrated a weak bands in low frequency region expanded between 500 and 600 cm⁻¹ which are attributed to bending vibrations of Bi–O–Bi bonds in highly distorted BiO₆ octahedral units [26,27]. From the IR spectra, it is evident that, the centres of the 750–1100 cm⁻¹ and 1150–1500 cm⁻¹ bands in bismuth-containing glass were slightly shifted to lower wave numbers with reduced width compared to lead-containing sample. It has been highlighted that, the center of the



Fig. 3. Optical absorption spectra of lead- (a), and bismuth- (b) containing glasses. In the figure, the vertical lines representing the wavelengths selected for NLO measurements.

band around 750–1100 cm⁻¹ shifted to lower wave number indicates an increase in NBOs, and a longer bond length of BO₄ structural unit. While, the center of the same band shifted to higher wave number indicating a decrease in NBOs and a shortening in the bond length of BO₄ [27]. Therefore, the shift of 760–1100 cm⁻¹ band to lower wave numbers is

attributed to increase in NBOs and a lengthening in the bond length of BO_4 when Bi_2O_3 incorporated in the place of PbO. Further, the shift of 1150–1500 cm⁻¹ band towards the lower wave numbers in Bi_2O_3 -containing sample may be due to the fact that, the new bridging bond of Bi–O–B is formed by the inducement of strongly polarizing Bi³⁺ ions.



Fig. 4. FTIR spectra of Eu₂O₃ free LPb50B and LBi50B glasses.

Since the stretching force constant of Bi–O bonding is substantially lower than that of the Pb–O, hence the stretching frequency of Bi–O–B might trend to be lower [26,28,29]. The refractive index, polarizability of all the investigated glasses are calculated and are furnished in Table 1 along with Eu³⁺ ion concentration.

NLO attributes (the absorption and refraction) of the glasses were investigated with the aid of OA and CA Z-scan experiments respectively. In CA mode the aperture in the far field was set partially closed i.e. the aperture was set open by 40%, to let only the center of the spot at far field pass to the detector. Fig. 5 (a) and (b) represent the OA Z-scan signatures of LPb50BEux and LBi50BEux glasses at 800 nm respectively. All the examined glass samples demonstrated a broad and downward valley at Z = 0 in the OA measurement at all the excitation wavelengths as shown in Fig. 5, revealing the feature of reverse saturable absorption (RSA) type of nonlinearity present in the studied glasses [30]. The similar features for all the samples irrespective of excitation wavelengths. This RSA kind of nonlinearity is the characteristic feature for optical limiting property, a property that is widely applicable in the protection of optical sensors and other sensitive devices. The CA Z-scan signatures LPb50BEux and LBi50Eux glasses at 800 nm are depicted in Fig. 6 (a) and (b), respectively. The valley-peak configuration noticed in Fig. 6 correspond to a positive nonlinear refractive index and is characteristic of self-focusing behaviour of the glass samples for the propagating light [17]. Similar signatures were observed at all the excitation

wavelengths for all the samples.

The measured Z-scan data in OA Z-scan mode of all studied glasses are well fitted with two photon absorption (2PA) equation found in Refs. [31] shown by solid lines in Fig. 5. The experimentally collected CA Z-scan data were fitted with the theoretical equation (solid lines in Fig. 6) [17] to obtain the phase difference value ($\Delta \Phi_0$). Using the obtained $\Delta \Phi_0$ the nonlinear refractive index (n_2) values are evaluated using the formula

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

where I_{00} is the input laser light peak intensity and L_{eff} is the effective path length of light propagation in the sample and λ be the excitation wavelength. The variations of 2 PA coefficient (α_2) with respect to spectral excitation for the LPb50BEux and LBi50BEux glasses are shown in Fig. 7 (a) and (b), respectively. Similarly, the attenuations of n_2 in LPb50BEux and LBi50BEux glasses with reference to spectral excitation are represented, respectively, in Fig. 8 (a) and (b). From the figures, it is evident that the α_2 is increased as the Eu₂O₃ content increased from 0.5 mol% to 2 mol% in the studied glasses. It is also evident from the figure that the α_2 is increasing as the excitation wavelength is shifted towards blue side. It has been demonstrated that, when the energy of excitation wavelength approaches the optical bandgap energy of the glasses

Table 1

				1 - 34	1 1 1 1 1 0	1 81 0		1 .1		
Physical and	optical i	properties of	11n-doped	and En ^{or}	doned PbO	and BloOa	containing	lanthaniim	borate a	glasses
ingorear and	optical	properties of	an aopea	and Da	aopea i bo	una 21203	containing		Dorace ,	0-400000

	1	2 3	0	U				
Properties (±error limits)	LPb50B	LPb50Eu0.5	LPb50BEu1	LPb50BEu2	LBi50B	LBi50Eu0.5	LBi50Eu1	LBi50Eu2
Density, ρ (g·cm ⁻³) (±0.002) Molar Volume, V _m (cm ³ ·mol ⁻¹) (±0.001)	5.393 29.05	5.36 29.45	5.103 31.25	5.043 32.18	6.812 43.071	6.795 43.387	5.808 50.996	5.940 50.339
Molar Refractivity, R_M (cm ⁻³) (±0.002) Electronic Polarizability, α_e (×Å ³) (±0.001)	12.40 4.912	12.60 4.991	13.50 5.352	14.20 5.631	22.701 8.996	22.934 9.089 2.080	27.774 11.00 2.142	27.843 11.032
Explored block, if (± 0.001) Direct optical band gap, E_g^{dir} (eV) (± 0.002)	2.812	2.866	2.770 2.439	1.834 2.634 2.188	2.084 2.623 2.373	2.089 2.551 2.314	2.142 2.515 2.268	2.325
Concentration of Eu ₂ O ₃ (mol%) Eu ³⁺ concentration, N ($\times 10^{22}$ ions/cm ³) (±0.001)	0	0.5 0.93	1 1.75	2.100 2 3.41	0	0.5 0.694	1 1.181	2.392



Fig. 5. Open aperture Z-scan profiles of (a) lead-containing glass samples and (b) bismuth-containing glass samples at 800 nm. Solid symbols represent the experimentally measured Z-scan data and solid lines are the theoretical fits to the data points.

resulted in enhancement in optical nonlinearity due to resonant effect [32]. Therefore, in the current examination the enhancement in a_2 as the excitation wavelength approaches the optical bandgap energy is attributed to resonance effect. Further, the figures clearly demonstrate that the n_2 values are independent of excitation wavelength (nearly the n_2 values are constant considering the experimental error), while the n_2 values are increased with increase in Eu₂O₃ content in the glass composition. The real and imaginary parts and hence total third order NLO susceptibility ($\chi^{(3)}$) values are calculated by utilizing the expressions [17]. All the values evaluated are furnished in Table 2. The error bars attached to the experimentally measured data arise from Z-scan noises, inhomogeneous glass samples etc. Typically, errors are estimated on a level of 2% for OA Z-scan data and 5% for CA Z-scan data.

4. Discussion

In the examined glasses, there were no absorption peaks in the 750–1000 nm region as evidenced from the UV–Visible absorption spectra. Therefore, the resonant and/or energy transfer mechanisms are ruled out for the observed optical nonlinearities in the studied glasses. The positive (reverse saturable absorption in OA and valley-peak signature in CA configurations) non-resonant type optical nonlinearity in studied glasses is attributed to both NBOs and polarizability of the glasses based on the following arguments. The optical band gap values and refractive indices of the prepared glasses were measured. The optical bandgap decreased from 2.866 to 2.634 eV and from 2.551 to 2.325 eV respectively in lead- and bismuth-containing samples, while the indirect optical band gap values decreased from 2.575 to 2.188 eV in lead-containing glasses and from 2.314 to 2.136 eV in bismuth-comprising



Fig. 6. Closed aperture Z-scan profiles of (a) lead-containing glass samples and (b) bismuth-containing glass samples measured at 800 nm. Solid symbols represent the experimentally measured Z-scan data and solid lines are the theoretical fits to the data points.

glasses when the Eu³⁺ content increased from 0.5 to 2 mol%. The refractive index values increased from 1.801 to 1.834 in lead-containing samples and from 2.089 to 2.171 in bismuth-containing samples as the Eu³⁺ concentration raised from 0.5 to 2 mol%. These attenuations clearly tell that the NBOs (O₂²⁻) are increasing with increase in Eu³⁺ ions concentration in the glass matrix. It has been explained, that the NBOs (O₂²⁻) are weakly and less covalently bonded to the network cations, whose valence electrons can be easily distorted and resulted in high charge displacements when subjected to the optical electric field. Hence a strong anharmonic effect arises from the NBOs [33]. Therefore, the NLO susceptibility increased with increase in Eu³⁺ concentration. In addition to the NBOs, the outer valence electrons present in outermost electronic shell of Eu³⁺ ions to be distorted when glasses are irradiated with optical electric field (electric field component of laser light). Therefore, large charge displacements are produced which causes the

large hyperpolarizability of the Eu³⁺ ions. It has been reported, that the electronic polarizability affects the NLO properties of glasses. In support of this, the electronic molar polarizability (α_e) values were calculated for all the studied glasses using the relation [16] and are furnished in Table 1.

$$\alpha_{e} = \frac{3}{4\pi N_{A}} (R_{M})$$
⁽²⁾

where N_A is Avogadro's number and R_M is the molar refraction value and is given by [16].

$$R_{\rm M} = \frac{\varepsilon - 1}{\varepsilon + 2} \left[V_{\rm m} \right] \tag{3}$$

in which ε be the dielectric constant ($\varepsilon = n^2$, n is refractive index) and V_m is average molecular weight/density of the glasses. From Table 1 it can



Fig. 7. Variations of 2 PA coefficient as a function of excitation wavelength for the (a) PbO comprising glasses and (b) Bi₂O₃ comprising glasses.

be identified that, the electronic polarizability values showed increase tendency from 4.991 to 5.631 Å³ in LPb50BEux glass samples and from 9.089 to 11.032 Å³ in LBi50BEux glasses with Eu³⁺ content increase from 0.5 to 2 mol% in the glass composition. This fact concludes the enhancement in nonlinear optical susceptibility of the glasses is ascribed to the polarizability of the glasses, which in turn is dependent to the increase in of the Eu³⁺ ion content. The increase of the electronic polarizability magnitudes is attributed to the presence of Eu³⁺ (1.12 Å³) ions and the incorporation of Eu³⁺ (1.12 Å³) ions for B³⁺ (0.003 Å³) in the composition whose polarizability is less than Eu³⁺ [13,34]. The similar behaviour has been observed in BiCl₃–Li₂O–B₂O₃–Er₂O₃ glasses, and in CaO–B₂O₃–Al₂O₃–CaF₂-Nd₂O₃ glasses in which the polarizability showed a constant increase with the Er³⁺ and Nd³⁺ content respectively

[35,36].

Further, the $\chi^{(3)}$ is related to linear susceptibility as [37].

$$\chi^{(3)} = \left(\chi^{(1)}\right)^4 \times 10^{-10} (esu) \tag{4}$$

According to Harmonic Oscillator model $\chi^{(1)}$ can be expressed as [37].

$$\chi^{(1)}(\omega) = \frac{Nq^2}{m(\omega_0^2 - \omega)} \tag{5}$$

in which *N* is the Eu³⁺ ion concentration, *q* is the charge, *m* is the electron mass, ω is the incident frequency and ω_0 is the resonant frequency. The Eu³⁺ ion concentration has been attained using the



Fig. 8. Variation of n_2 with respect to the excitation wavelength for the (a) lead-containing glasses and (b) bismuth-containing glasses.

expression found in Refs. [38] and furnished in Table 1. From Table 1 it can be seen that the Eu^{3+} ion concertation is constantly increased as a function of Eu³⁺ content. Therefore, the linear susceptibility is increased as it is directly related to Eu^{3+} ion concentration through equation (4) which in turn probably increases the third-order nonlinear susceptibility. With all these explanations, we conclude that both the NBOs and polarizability of the glasses are contributing for the observed optical nonlinearity in glasses. Further, from Table 1 it can be seen that, the α_2 , n_2 and hence $\chi^{(3)}$ are high for the LBi50BEux glasses than for LPb50BEux glasses. Since the polarizability values of Bi2O3-framed glass samples are high compared PbO-comprising glasses. The FTIR analysis clearly revealed that NBOs content is more in LBi50B glass than LPb50B glass. Therefore, the nonlinear parameters are quite high in Bi₂O₃-comprising glasses than PbO-containing glasses. In addition, the greatness of $\chi^{(3)}$ in Bi₂O₃ comprising glasses is also due to the fact that, the intensity dependent n_2 is related to bond lengths present in the glass network according to the below equation [39].

$$n_2 = \frac{2.5 \times 10^{-12} f_L^3 (n^2 - 1) d^2 E_s^6}{n (E_s^2 - E^2)^4} (esu)$$
(7)

where f_L is the Lorentz field factor, n is the intensity-independent refractive index, E_S is the Sellmeier gap, E is the photon energy and d is the M–O bond length (M: cation). In the PbO-comprising glasses the Pb–O bond lengths are in the range of 2.18–2.49 Å while in Bi₂O₃-containing glasses the Bi–O bond lengths are in the range of 2.08–2.80 Å

[40]. Due to this elongated Bi–O bond lengths the n_2 and hence $\chi^{(3)}$ values are greater for LBi50BEx glasses compared to LPb50BEux glasses.

Further, Lin et al. [41] have examined the nonlinear optical response time of silicate glasses through the optical Kerr shutter experiment with 30 fs laser pulses and the estimated response time was less than 90 fs. Sugimoto et al. [42] have investigated the temporal dynamics of glasses via degenerate four-wave mixing method using 200 fs laser pulses and the electronic response of their examined glasses below 200 fs. Similarly, Yu et al. [43] have investigated the NLO properties of HMO glasses by means of the optical Kerr gate method and temporal response was faster than 350 fs. Their results clearly suggested that the observed nonlinearity arises predominantly from electronic polarization. The Z-scan experiments are single-beam experiments in which the pumping and probing of the glass samples are done by the same laser pulses. Hence, by the analogy the response time of glasses studied in the present investigation has ultrafast component. However, in the present study the NLO measurements were performed using fs laser pulses produced at 80 MHz repetition rate. Because of this high repetition rate, there will be a component of thermal effect (heating of the sample) in the observed nonlinearity [44]. However, investigations need be undertaken with fs, kHz repetition pulses to separate out the pure electronic contribution, which will be a part of our future works.

The figure of merit (F) is a peculiar propriety which decides the suitability of the glasses for NLO device application and is given by F = $2\alpha_2\lambda/n_2$ where, the terminologies have their usual meanings. When the F < 1 is holds good, then the glasses could be utilized for switching applications, whereas the F > 1 is matches, then the glasses are beneficial in nonlinear optical limiting applications. In the current study, all the investigated glasses satisfied the F > 1 condition. Nonetheless, enhancement in α_2 , n_2 and hence $\chi^{(3)}$ as a function of Eu₂O₃ clearly suggest that the examined glasses activated with high concentration of Eu₂O₃ (2 mol%) are beneficial for optical limiting applications in the studied wavelength region to protect the human eyes and sensitive photonic devices from high energy laser radiations. The α_2 and n_2 values of the studied glasses are greater compared to those reported for Sm³⁺ [11] and Gd³⁺ [9] activated borate glasses. Nonetheless, the values are lesser than those reported for bismuth-containing zinc borate glasses [45] and alkaline earth bismuth borate glasses [46]. For comparison, the NLO coefficients of certain glass systems are provided in Table 3.

5. Conclusions

Eu³⁺-doped borate glasses containing high concentration of heavy metal oxides (PbO and Bi₂O₃) have been designed by utilizing melt quench technique. The NLO properties of glasses were measured by means of Z-scan technique. The OA Z-scan signatures exhibited RSA nonlinearity due to 2PA while the CA Z-scan profiles demonstrated a positive nonlinear refraction attributed to self-focusing effect. The a_2 , n_2 and $\chi^{(3)}$ values showed an increase trend as a function of Eu₂O₃ content. The enhancements are attributed to NBOs generated when Eu³⁺ incorporated to the glass composition and hyperpolarizability of Eu³⁺ ions. The NLO properties and their evaluations suggest the glasses containing high concentration of Eu³⁺ are beneficial for NLO devices particularly for optical limiting applications in the near IR region. Further, compared to PbO-containing glasses the Bi₂O₃ containing glasses demonstrated strong optical nonlinearities due to the presence of high NBOs content as evidenced by FTIR spectra.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 2

Summary of NLO results studied glasses viz., the 2 PA coefficient (α_2), nonlinear refractive index (n_2), nonlinear optical susceptibility [$\chi^{(3)}$] and figure of merit (F) values at near IR spectral regions under fs regime.

Glass labels	LPb50B	LPb50BEu0.5	LPb50BEu1	LPb50BEu2	LBi50B	LBi50BEu0.5	LBi50BEu1	LBi50BEu2
→ NLO parameters								
\perp								
•								
$\lambda = 750 \text{ nm}$								
α_2 (× 10 ⁻¹¹ m/W)	1.03	1.06	1.17	1.27	1.05	1.13	1.24	1.45
$n_2 (\times 10^{-18} \text{ m}^2/\text{W})$	1.08	1.19	1.32	1.68	1.09	1.27	1.42	1.74
$\text{Re}\chi^{(3)}$ (\times 10 ⁻¹³ esu)	8.15	9.76	10.99	13.89	12.10	14.03	16.49	20.76
$Im\chi^{(3)}$ (\times 10 ⁻¹³ esu)	5.01	5.22	5.80	6.48	6.92	7.45	8.61	10.37
$\chi^{(3)}$ ($ imes$ 10 ⁻¹³ esu)	10.12	11.07	12.43	15.33	13.94	15.89	18.61	23.21
F	14.31	13.36	13.30	11.34	14.45	13.35	13.10	12.50
$\lambda = 800 \text{ nm}$								
α_2 (× 10 ⁻¹¹ m/W)	0.99	1.03	1.13	1.23	1.08	1.11	1.22	1.33
n_2 ($\times 10^{-18}$ m ² /W)	1.07	1.18	1.31	1.62	1.09	1.26	1.41	1.74
$\text{Re}(3)$ (\times 10 ⁻¹³ esu)	8.74	9.75	10.93	13.86	12.05	13.99	16.44	20.75
$Im\chi^{(3)}$ (\times 10 ⁻¹³ esu)	5.15	5.41	6.02	6.67	7.60	7.86	9.02	10.12
$\chi^{(3)}$ ($ imes$ 10 ⁻¹³ esu)	10.14	11.15	12.48	15.38	14.25	16.05	18.75	23.09
F	14.80	13.97	13.80	12.15	15.85	14.10	13.84	12.23
$\lambda = 850 \text{ nm}$								
$\alpha_2 (\times 10^{-11} \text{ m/W})$	0.98	1.02	1.13	1.22	1.02	1.11	1.21	1.32
$n_2 (\times 10^{-10} \text{ m}^2/\text{W})$	1.08	1.18	1.31	1.62	1.09	1.26	1.41	1.73
$\text{Re}^{(3)}(\times 10^{-13} \text{ esu})$	8.77	9.72	10.89	13.84	12.08	13.99	16.42	20.72
$Im\chi^{(3)}$ (× 10 ⁻¹³ esu)	5.39	5.69	6.37	7.04	7.56	8.31	9.57	10.65
$\chi^{(3)}$ ($ imes$ 10 ⁻¹³ esu)	10.30	11.26	12.62	15.52	14.24	16.27	19.00	23.29
F	15.43	14.69	14.66	12.80	15.91	14.98	14.59	12.97
$\lambda = 900 \text{ nm}$								
α_2 (× 10 ⁻¹¹ m/W)	0.96	1.01	1.11	1.20	1.01	1.10	1.20	1.29
$n_2 (\times 10^{-10} \text{ m}^2/\text{W})$	1.07	1.18	1.31	1.62	1.09	1.27	1.41	1.73
$\text{Re}^{(3)}$ ($\times 10^{-13}$ esu)	8.74	9.72	10.92	13.84	12.11	14.04	16.39	20.70
$\lim_{x \to 1} (1) (\times 10^{-13} \text{ esu})$	5.59	6.14	6.64	7.35	7.96	8.74	10.03	11.13
$\chi^{(0)}$ (× 10 ⁻¹³ esu)	10.37	11.49	12.78	15.668	14.49	16.55	19.22	23.51
F	16.15	15.41	15.25	13.33	16.68	15.59	15.32	13.42
$\frac{\lambda = 950 \text{ nm}}{10^{-11} \text{ m (m)}}$	0.04	1.01	1 10		0.00	1.00	1 1 1	1.00
$\alpha_2 (\times 10^{-18} \text{ m/W})$	0.94	1.01	1.10	1.11	0.99	1.09	1.11	1.28
\underline{n}_2 (× 10 m/W) \underline{n}_2 (3) (~ 10 ⁻¹³ cm)	1.08	1.18	1.31	1.62	1.09	1.20	1.41	1./3
$Re\chi^{(3)}$ (× 10 esu)	8.79	9.70	10.91	13.84	12.11	13.96	16.39	20.67
$V_{(3)}^{(3)}$ ($\times 10^{-13}$ esc.)	5.80	0.20	0.90	7.18	8.26	9.11	9.83	11.51
$X^{(1)}$ (× 10 · esu)	10.52	11.55	12.95	13.39	14.00	10.08	19.12	23.00
F 1000 mm	10.54	10.20	15.95	13.02	17.20	10.44	14.90	14.06
A = 1000 nm A = 1000 nm	0.02	0.00	1.00	1.01	0.05	1.01	1.10	1.02
M_2 (× 10 m/w)	1.92	0.99	1.00	1.01	0.95	1.01	1.10	1.20
W_2 (× 10 III / W) $P_{0W}^{(3)}$ (× 10 ⁻¹³ out)	1.05	1.12	1.55	1.01	11.07	12.00	1.41	1./2
$rec (\times 10^{-13} \text{ esu})$	5.09	9.20	6.60	13.70	11.04	13.90	10.37	20.39
$V^{(3)}(\times 10^{-13} \text{ esc})$	0.98 10.45	0.52	13 10	0.00	0.30 14.46	0.92	10.22	11.70
r (× 10 esu)	17 50	11.32	13.10	10.09	14.40	16.02	19.30	23.00
F	17.52	1/.08	14.81	12.33	1/./0	10.03	15.00	14.30

Table 3

NLO Coefficients of certain selected glass systems.

Glass composition	Excitation wavelength and other details	a_2 ($ imes$ 10 ⁻¹¹ m/W)	n_2 ($ imes$ 10 ⁻¹⁸ m ² /W)	Reference
{[(TeO ₂) ₇₀ (B ₂ O ₃) ₃₀] ₇₀ (ZnO) ₃₀ } _{1-x} (Gd ₂ O ₃) _x , $x = 1 \text{ mol}\%$	532 nm (5 ns, 10 Hz)	0.6157	0.9425	[10]
{[(TeO ₂) ₇₀ (B ₂ O ₃) ₃₀] ₇₀ (ZnO) ₃₀ } _{1-x} (Gd ₂ O ₃) _x , $x = 2 \text{ mol}\%$		0.7117	0.6317	[10]
$\{[(TeO_2)_{70}(B_2O_3)_{30}]_{70}(ZnO)_{30}\}_{1-x} (Gd_2O_3)_x, x = 3 \text{ mol}\%$		0.7466	0.7217	[10]
{[(TeO ₂) ₇₀ (B ₂ O ₃) ₃₀] ₇₀ (ZnO) ₃₀ } _{1-x} (Gd ₂ O ₃) _x , $x = 4 \text{ mol}\%$		0.7142	0.8227	[10]
$\{[(TeO_2)_{70}(B_2O_3)_{30}]_{70}(ZnO)_{30}\}_{1-x} (Gd_2O_3)_x, x = 5 \text{ mol}\%$		0.6460	0.8275	[10]
xSm_2O_3 -(100- x) [0.1BaO-0.4ZnO-0.5B ₂ O ₃] with $x = 0.0$ mol%	532 nm (5 ns, 10 Hz)	0.00572	0.000106	[12]
xSm_2O_3 -(100- x) [0.1BaO-0.4ZnO-0.5B ₂ O ₃] with $x = 0.5$ mol%		0.001128	0.00847	[12]
xSm_2O_3 -(100- x) [0.1BaO-0.4ZnO-0.5B ₂ O ₃] with $x = 1 \text{ mol}\%$		0.001507	0.00986	[12]
xSm_2O_3 -(100- x) [0.1BaO-0.4ZnO-0.5B ₂ O ₃] with $x = 1.5$ mol%		0.001928	0.01022	[12]
xSm2O3–(100– x) [0.1BaO–0.4ZnO–0.5B ₂ O ₃] with $x = 2.0$ mol%		0.002746	0.011299	[12]
45Bi ₂ O ₃ -30ZnO-25B ₂ O ₃	800 nm (110 fs, 1 kHz)	1.04	0.15	[45]
45Bi ₂ O ₃ -30ZnO-25B ₂ O ₃	532 nm (30 ps, 10 Hz)	24.6	-	[45]
10CaO-35Bi ₂ O ₃ -55B ₂ O ₃	800 nm (110 fs, 1 kHz)	0.028	-	[46]
10CaO-35Bi ₂ O ₃ -55B ₂ O ₃	532 nm (30 ps, 10 Hz)	1.3	-	[46]
10 SrO -35 Bi $_2$ O $_3-55$ B $_2$ O $_3$	800 nm (110 fs, 1 kHz)	0.034	-	[46]
10SrO-35Bi ₂ O ₃ -55B ₂ O ₃	532 nm (30 ps, 10 Hz)	2.4	-	[46]

CRediT authorship contribution statement

P. Ramesh: Writing - original draft. Vinod Hegde: Writing - original

draft. A.G. Pramod: Data curation. B. Eraiah: Conceptualization. S. Venugopal Rao: Formal analysis, Conceptualization. S. Shisina: Formal analysis, Conceptualization. Subrata Das: Writing - original

draft, Writing - review & editing. **D.A. Agarkov:** Formal analysis. **G.M. Eliseeva:** Formal analysis. **G. Jagannath:** Supervision, Writing - original draft. **M.K. Kokila:** Supervision, Formal analysis.

Acknowledgements

The primary author (PR) is thankful to late Dr. Rajan V. Anavekar, Former Professor, Department of Physics, Bangalore University, Bangalore, for useful discussions and valuable suggestions. The authors PR and GJ are grateful to Dr. Amarnath R. Allu, Scientist, CSIR-CGCRI, Kolkata for constructive suggestions. SVR thanks DRDO for continuous financial support through ACRHEM. The author SS acknowledges CSIR, New Delhi for the award of Junior Research Fellowship.

References

- [1] C. Wang, G. Shi, Z. Zhu, S. Luo, W. Sun, W. Jiao, R. Gao, G. Fan, Y. Song, Opt. Mater. 100 (2020) 109621.
- [2] H. Nakamura, Y. Sugimoto, K. Kanamoto, N. Ikeda, Y. Tanaka, Y. Nakamura, S. Ohkouchi, Y. Watanabe, K. Inoue, H. Ishikawa, K. Asakawa, Optic Express 12 (2004) 6606–6614.
- [3] W. Chen, K.M. Beck, R. Bücker, M. Gullans, M.D. Lukin, H. Tanji-Suzuki, V. Vuletić, Science 341 (2013) 768–770.
- [4] T. Terashima, K. Shimoto, T.H. Yoko, Phys. Chem. Glasses 38 (1997) 211-217.
- [5] C. Chen, R. Li, Int. Rev. Phys. Chem. 8 (1988) 65–91.
- [6] M. Luo, Y. Song, F. Liang, N. Ye, Z. Lin, Inorg. Chem. Front. 5 (2018) 916–921.
 [7] S.N.C. Santos, J.M.P. Almeida, K.T. Paula, N.B. Tomazio, V.R. Mastelaro, C.
- R. Mendonça, Opt. Mater. 73 (2017) 16–19.
 [8] R. Miedzinski, I. Fuks-Janczarek, M. Reben, Y. El Sayed Said, Opt. Mater. 85 (2018)
- [6] R. Miledziniski, I. Puks-Janczarek, M. Reben, T. Er Sayed Said, Opt. Mater. 85 (2016) 48–54.
- [9] C. Eevon, M.K. Halimah, A. Zakaria, C.A.C. Azurahanim, M.N. Azlan, M.F. Faznny, Results Phys 6 (2016) 761–766.
- [10] G. Jagannath, B. Eraiah, K.N. Krishnakanth, S. Venugopal Rao, in: AIP Conf. Proc. vol. 2142, 2019, 070024-070028.
- [11] K. Nanda, R.S. Kundu, S. Sharma, D. Mohan, R. Punia, N. Kishore, Solid State Sci. 45 (2015) 15–22.
- [12] A.G. Pramod, C.G. Renuka, Y.F. Nadaf, R. Rajaramakrishna, J. Mol. Liq. 292 (2019) 111383.
- [13] S.N.C. Santos, K.T. Paula, J.M.P. Almeida, A.C. Hernandes, C.R. Mendonça, J. Non-Cryst. Solids 524 (2019) 119637.
- [14] E. Furet, K. Costuas, P. Rabiller, O. Maury, J. Am. Chem. Soc. 130 (2008) 2180–2183.
- [15] G. Jagannath, B. Eraiah, K. Jayanthi, S.R. Keshri, S. Som, G. Vinitha, A.G. Pramod, K.N. Krishnakanth, G. Devarajulu, S. Balaji, S. Venugopal Rao, K. Annapurna, S. Das, A.R. Allu, Phys. Chem. Chem. Phys. 22 (2020) 2019–2032.
- [16] G. Jagannath, B. Eraiah, K. NagaKrishnakanth, S. Venugopal Rao, J. Non-Cryst. Solids 482 (2018) 160–169.

- [17] G. Jagannath, B. Eraiah, A. Gaddam, H. Fernandes, D. Brazete, K. Jayanthi, K. N. Krishnakanth, S. Venugopal Rao, J.M.F. Ferreira, K. Annapurna, A.R. Allu, J. Phys. Chem. C 123 (2019) 5591–5602.
- [18] C.R. Kesavulu, K.K. Kumar, N. Vijaya, K.S. Lim, C.K. Jayasankar, Mater. Chem. Phys. 141 (2013) 903–911.
- [19] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4424-4442.
- B.C. Jamalaiah, L.R. Moorthy, H.J. Seo, J. Non-Cryst. Solids 358 (2012) 204–209.
 P. Limkitjaroenporn, J. Kaewkhao, P. Limsuwan, W. Chewpraditkul, J. Phys. Chem.
- Solid. 72 (2011) 245–251. [22] E.I. Kamitsos, M.A. Karakassides, G.D. Chryssikos, J. Phys. Chem. 91 (1987)
- 1073–1079. [23] B.V.R. Chowdari, Z. Rong, Solid State Ionics 90 (1996) 151–160.
- [24] E.I. Kanitsos, A.P. Patsis, M.A. Karakassides, G.D. Chryssikos, J. Non-Cryst. Solids 126 (1990) 52–67.
- [25] I. Kashif, A. Abd El-Maboud, R. El-Said, E.M. Sakr, A.A. Soliman, J. Alloys Compd. 539 (2012) 124–128.
- [26] Y. Cheng, H. Xiao, W. Guo, W. Guo, Thermochim. Acta 444 (2006) 173-178.
- [27] Y.B. Saddeek, M.S. Gaafar, Mater. Chem. Phys. 115 (2009) 280–286.
- [28] Y.B. Saddeek, M.S. Gaafar, S.A. Bashier, J. Non-Cryst. Solids 356 (2010) 1089–1095.
- [29] Y. Cheng, H. Xiao, W. Guo, W. Guo, Ceram. Int. 33 (2007) 1341–1347.
- [30] J. Yi, S. Lu, L. Miao, T. Xie, C. Zhao, J. Li, Y. Pan, Opt. Mater. 98 (2019) 109435.
- [31] J. Gangareddy, E. Bheemaiah, V. Gandhiraj, J.T. James, J.K. Jose, K. Katturi Naga, V.R. Soma, Appl. Phys. B Laser Optic. 124 (2018) 1–9.
- [32] J.M.P. Almeida, L. De Boni, A.C. Hernandes, C.R. Mendonça, Optic Express 19 (2011) 17220–17225.
- [33] X. Zhu, Q. Li, N. Ming, Z. Meng, Appl. Phys. Lett. 71 (1997) 867-869.
- [34] X. Zhao, X. Wang, H. Lin, Z. Wang, Phys. B Condens. Matter 392 (2007) 132–136.
 [35] G. Chandrashekaraiah, N. Sivasankara Reddy, B. Sujatha, R. Viswanatha,
- C. Narayana Reddy, J. Non-Cryst. Solids 498 (2018) 252–261. [36] J.D.M. Dias, G.H.A. Melo, E.C. Paz, T.A. Lodi, M.J. Barboza, A. Steimacher,
- F. Pedrochi, Int. J. Appl. Glass Sci. 9 (2018) 428–434.
- [37] H. Nasu, J. Matsuoka, O. Sugimoto, M. Kida, K. Kamiya, J. Ceram. Soc. Japan 101 (1993) 43–47.
- [38] G. Jagannath, B. Eraiah, K. Jayanthi, S.R. Keshri, S. Som, G. Vinitha, A.G. Pramod, K.N. Krishnakanth, G. Devarajulu, S. Balaji, S. Venugopal Rao, K. Annapurna, S. Das, A.R. Allu, Phys. Chem. Chem. Phys. 22 (2020) 2019–2032.
- [39] S.-H. Kim, T. Yoko, J. Am. Ceram. Soc. 78 (1995) 1061-1065.
- [40] Y.G. Choi, K.H. Kim, V.A. Chernov, J. Heo, J. Non-Cryst. Solids 259 (1999) 205–211.
- [41] T. Lin, Q. Yang, J. Si, T. Chen, F. Chen, X. Wang, X. Hou, K. Hirao, Optic Commun. 275 (2007) 230–233.
- [42] N. Sugimoto, K. Hirao, H. Kanbara, S. Fujiwara, K. Tanaka, Opt. Lett. 21 (1996) 1637–1639.
- [43] B.L. Yu, A.B. Bykov, T. Qiu, P.P. Ho, R.R. Alfano, N. Borrelli, Optic Commun. 215 (2003) 407–411.
- [44] A. Gnoli, L. Razzari, M. Righini, Optic Express 13 (2005) 7976–7981.
- [45] B. Shanmugavelu, V.V.R.K. Kumar, R. Kuladeep, D.N. Rao, J. Appl. Phys. 114 (2013) 243103–243108.
- [46] M.V. Rao, V.V. Ravi Kanth Kumar, N.K. Shihab, D.N. Rao, Optic Laser. Technol. 107 (2018) 110–115.