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# Structural and Femtosecond Third-Order Nonlinear Optical **Properties of Sodium Borate Oxide Glasses: Effect of Antimony**

Gangareddy Jagannath,<sup>†,#</sup> Bheemaiah Eraiah,<sup>\*,†</sup> Anuraag Gaddam,<sup>‡,#</sup> Hugo Fernandes,<sup>‡</sup> Daniela Brazete,<sup>‡</sup> K. Jayanthi,<sup>§</sup><sup>®</sup> Katturi Naga Krishnakanth,<sup>||</sup> Soma Venugopal Rao,<sup>||</sup> José M. F. Ferreira,<sup>\*,‡</sup><sup>®</sup> K. Annapurna,<sup>⊥</sup> and Amarnath R. Allu<sup>\*,⊥</sup><sup>®</sup>

<sup>†</sup>Department of Physics, Bangalore University, 560056 Bengaluru, Karnataka, India

<sup>‡</sup>Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>§</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, 560012 Bengaluru, Karnataka, India

<sup>||</sup>Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, 500046 Hyderabad, Telangana, India

 $^{\perp}$ Glass Division, CSIR-Central Glass and Ceramic Research Institute, 700032 Kolkata, India

ABSTRACT: Structural and optical properties of antimony-containing sodium borate glasses were studied and their ultrafast third-order nonlinear optical (NLO) properties have been evaluated using Z-scan measurements with femtosecond (fs) pulses (~150 fs, 80 MHz) at 750, 800, and 880 nm wavelengths. Glasses in the (mol %)  $20Na_2O - (80 - x)B_2O_3 - xSb_2O_3$ (where x = 0, 10, 20, and 30) system have been fabricated via melt quench technique. The structural modifications were analyzed using the Raman and magic angle spinning (MAS)-nuclear magnetic resonance (NMR)  $(^{11}B)$ MAS-NMR and <sup>23</sup>Na MAS-NMR) techniques. The optical absorption spectra revealed that the absorption edge was red-shifted, suggesting the decrease in band gap energy with increase of antimony content in the glasses. Raman scattering results revealed that the boroxol rings are depressed with the incorporation of Sb<sub>2</sub>O<sub>3</sub> for replacing B<sub>2</sub>O<sub>3</sub>. <sup>11</sup>B MAS-



NMR results showed a progressive increase of B<sup>4</sup> units at the expense of B<sup>3</sup> units. The Raman and <sup>11</sup>B MAS-NMR results support the formation of Sb<sup>5+</sup> ions due to oxidation of Sb<sup>3+</sup> that played the role of charge compensation. <sup>23</sup>Na MAS-NMR spectra revealed a decreasing trend in the average of bond lengths of Na-O with increasing Sb<sub>2</sub>O<sub>3</sub> contents. This suggested that sodium changed its role from charge compensator to modifier cation. The antimony-containing glasses demonstrated a reverse saturable absorption in open-aperture Z-scan mode due to two-photon absorption, while closed-aperture Z-scan signatures depicted positive nonlinear refraction due to self-focusing effect. The NLO coefficients were found to increase with Sb<sub>2</sub>O<sub>3</sub> due to the increased nonbridging oxygens and also due to the hyperpolarizability of Sb<sup>3+</sup> and Sb<sup>5+</sup> ions. The observed NLO data clearly suggest that the investigated glasses are beneficial for optical limiting applications.

# 1. INTRODUCTION

Glass materials over the years have drawn a special consideration due to their wide and ever-growing applications in lasers, optical fiber amplifiers, flat-panel displays, optical limiting and switching devices, optoelectronic and memory devices, solar cells, and light-emitting diodes, and in the biomedical field.<sup>1–3</sup> In the recent past, great attention has been paid to these materials for the development of optical devices and photonic components because of the ease of their fabrication and shaping.<sup>1</sup> Additionally, the vitreous materials possess many unique properties such as high transparency and high optical damage threshold. Several researchers have been working extensively on inorganic glasses to achieve strong nonlinear coefficients, which are essential parameters for the utilization of material in nonlinear optical (NLO) devices.<sup>4,5</sup> Among several types of glasses investigated, borate glasses have received huge attention owing to their low melting and glasstransition  $(T_g)$  temperatures, excellent physical-chemical properties, large coefficient of thermal expansion, and excellent optical properties.<sup>6</sup> To satisfy the various demands in technological applications, optimization of the chemical composition and knowledge on the role of each cation in the glass material is essential. Furthermore, understanding the correlation between the optical properties and structural characteristics of glasses is fundamental for the development of glass materials for NLO applications. The development of anionic group theory<sup>7</sup> has elucidated the structure-property relationship for NLO effects in inorganic materials based on perturbation theory for NLO susceptibilities of materials. According to the theory, the susceptibilities depend mainly on

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the boron-oxygen anionic group and their arrangement in space. Based on these considerations, among various existing  $(B_xO_y)^{z-}$  borate groups,  $(BO_3)^{3-}$ ,  $(BO_4)^{5-}$ ,  $(B_2O_5)^{4-}$ ,  $(B_2O_7)^{8-}$ ,  $(B_3O_6)^{3-}$ ,  $(B_3O_7)^{5-}$ ,  $(B_3O_8)^{7-}$ ,  $(B_3O_9)^{9-}$ ,  $(B_4O_9)^{6-}$ , and  $(B_5O_{10})^{5-}$  are of practical interest for designing new NLO devices.<sup>7,8</sup> It has been further reported that planar group with conjugated  $\pi$ -orbitals, such as  $(BO_3)^{3-1}$ and  $(B_3O_6)^{3-}$ , are favorable for large susceptibilities than the nonplanar tetrahedral  $(BO_4)^{5-}$  anionic groups with no conjugated  $\pi$ -orbital. In supporting this, the high-performance NLO properties from borate materials have been achieved due to the presence of isolated  $(BO_3)^{3-}$  groups.<sup>9</sup> Xue et al.<sup>10</sup> attempted to understand the effect of chemical bond on the NLO properties and postulated that due to highly localized electrons, (BO<sub>3</sub>)<sup>3-</sup> groups exhibit larger NLO coefficients compared to the  $(BO_4)^{5-}$  groups, which in general contain less localized electrons. To shed further light on this issue, a thorough and in-depth structural investigation is essential and would lead to the understanding of the local environment and spatial distribution of the network formers in glasses. Therefore, one needs to ascertain and evaluate the different coordination polyhedra present, as well as their corresponding linkages with each other.

Owing to their hyperpolarizabilities and the ability to create nonbridging oxygens (NBOs), the incorporation of heavymetal oxides (HMOs) such as Bi<sub>2</sub>O<sub>3</sub>, PbO, TeO<sub>2</sub>, GeO<sub>2</sub>, GaO<sub>2</sub>, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>3</sub>, etc. significantly alters the structure and properties of borate glasses.<sup>11-17</sup> They enhance the NLO properties of the borate glass to several orders of magnitude due to the greater polarizability of heavy-metal cations.<sup>18,19</sup> Shanmugavelu et al.<sup>4</sup> elucidated that the enhancement in third-order nonlinearity is due to the increase in BiO<sub>6</sub> groups containing NBOs with the increase of  $Bi_2O_3$  concentration in bismuth zinc borate glasses. Rao et al.<sup>18,19</sup> further demonstrated the effect of Bi2O3 on the NLO properties of borate glasses and obtained larger nonlinear effects due to the presence of hyperpolarizable anionic  $[BiO_4]^{5-}$  groups in borate glasses. It is interesting to note that utilization of composition-structure-property inter-relationship for different HMOs<sup>11-16</sup> in borate glasses is well documented. On the other hand, few reports<sup>17,20-24</sup> are available on utilizing the composition-structure-property relationship for Sb<sub>2</sub>O<sub>3</sub>-containing borate glasses to understand the observed NLO properties. It is well known that antimony(III) oxide, Sb<sub>2</sub>O<sub>3</sub>, is a good low-phonon and highrefractive-index HMO glass former.<sup>25</sup> Owing to the high polarizability and the presence of a stereochemically active lone pair of electrons, antimony-containing borate glasses are also considered as promising NLO materials.<sup>26</sup> Terashima et al.<sup>17</sup> studied the Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses and reported that the thirdorder nonlinear optical susceptibility  $[\chi^{(3)}]$  of binary borate glasses is enhanced with increasing Sb<sub>2</sub>O<sub>3</sub> content. Falcão-Filho et al.<sup>27</sup> demonstrated that the antimony orthophosphate glasses possess excellent nonlinear refractive index at 800 nm. Very recently, it has been observed that sodium borate glasses with a small amount (2 mol %) of antimony resulted in a small two-photon absorption (2PA) at 800 nm in femtosecond (fs) regime.<sup>28</sup> It is to be noted that the extent and ability of accepting high concentration of  $Sb_2O_3$  depends strongly on the type of glass network former.<sup>29</sup> Som et al.<sup>30</sup> have recently demonstrated that alkali borate glasses are truly exceptional since large amounts (>60 mol %) of Sb<sub>2</sub>O<sub>3</sub> can be incorporated without devitrification. Nevertheless, to the best

of our knowledge, borate glasses containing high concentration of Sb<sub>2</sub>O<sub>3</sub> have not been studied in great detail for NLO device applications. Furthermore, the structural modifications in the sodium borate network with the addition of Sb<sub>2</sub>O<sub>3</sub> have not been significantly explored. In view of the above, the present work aims at understanding the influence of Sb<sub>2</sub>O<sub>3</sub> on network structure of the sodium borate glasses. In addition, efforts have been made to study the influence of structural changes on their enhancement of fs NLO properties. The structure of glass materials was evaluated by Raman and magic angle spinning (MAS) nuclear magnetic resonance (NMR: for nuclei <sup>11</sup>B and <sup>23</sup>Na) spectroscopy techniques. The NLO properties were investigated using ~150 fs pulses in the wavelength region of 750–880 nm.

## 2. EXPERIMENTAL METHODS

2.1. Glass Preparation. The borate glass compositions  $20Na_2O - (80 - x)B_2O_3 - xSb_2O_3$  (NBS) (in mol %) with x varying between 0 and 30 mol % were synthesized through the conventional melt quenching technique. The samples were labeled as NBS-0, NBS-10, NBS-20, and NBS-30 corresponding to 0, 10, 20, and 30 mol % of Sb<sub>2</sub>O<sub>3</sub> concentration present in the glass compositions. The appropriate amounts of ARgrade starting materials such as sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99.99%, SD Fine), boric acid (H<sub>3</sub>BO<sub>3</sub>, 99.99%, SD Fine), and antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>, 99.99%, SD Fine) were weighed and mixed well. Finely ground starting materials were taken in porcelain crucibles and transferred to a high-temperature heating furnace (Heat Globe, Bengaluru). Initially, the batch was maintained at the temperature of 500 °C about 20 min for complete decarbonization; then, the temperature was raised slowly for melting the batch. Melting temperatures for compositions NBS-0, NBS-10, NBS-20, and NBS-30 were 1050, 940, 900, and 860 °C, respectively. The melts were quenched by pouring between two preheated brass molds. The NBS-0 glass was annealed at 470 °C (around the  $T_{\sigma}$  value), and the antimony-containing glasses were annealed at 350 °C for 4 h.

2.2. Physical and Optical Characterizations. The ultraviolet-visible-near-infrared (UV-vis-NIR) spectra of all of the polished samples were taken with the help of PerkinElmer Lambda-35 UV-visible spectrometer in the range of 200-1100 nm at room temperature with a resolution of 1 nm. The density measurements of all of the bulk glasses were carried out by employing Archimedes' principle (analytical balance, OHAUS, model: PAG 213). Refractive index (n) measurements were done using Abbe's refractometer with sodium vapor lamp (589.3 nm) as light source. For the refractive index (n) measurements, mono-bromonaphthalene was used as the contact layer between the sample and the prism of the refractometer. To quantify the contribution of Sb<sub>2</sub>O<sub>3</sub> to the NLO properties of borate glasses, the Z-scan technique<sup>31</sup> was employed. The nonlinear absorption and refraction measurements of glasses were performed in openaperture (OA) and closed-aperture (CA) configurations, respectively. For the NLO measurements, ~150 fs pulses delivered by a Ti:sapphire laser (Chameleon, M/s Coherent; operating in the 680-1040 nm spectral range) at a repetition rate of 80 MHz were utilized. The NLO measurements were performed at three spectral wavelengths of near-IR region, i.e., at 750, 800, and 880 nm. In Z-scan measurements, the highly polished bulk glass samples with thickness of ~1 mm were placed on a translation stage with 10  $\mu$ m resolution. A spatially

filtered input Gaussian laser beam of  $\sim 2$  mm diameter was focused on the samples with the help of 10 cm convex lens. During the experiment, the glass sample was moved along the propagation axis (symbolized as Z with Z = 0 as the focal point), and at each position, the sample experiences a different peak intensity. Therefore, the position-dependent output intensity (or transmission) of the laser beam was collected using a thermal sensor placed after the sample.

2.3. Structural Characterization. X-ray diffraction (XRD) profiles of all NBS glasses were collected with the help of PANalytical Empyrean X-ray diffractometer equipped with a PIXcel<sup>3D</sup> detector, using the Cu K $\alpha$  radiation (Cu K $\alpha_1$ source,  $\lambda = 0.15406$  nm, Cu K $\alpha_2$  source,  $\lambda = 0.154443$  nm). The nickel filter was used to filter Cu K $\beta$  line. Diffraction data were collected in the Bragg-Brentano geometry with the detector in the line scanning mode. The test samples were prepared by pressing the powdered glasses on an amorphous silicon substrate, and data were collected from 10 to  $80^\circ$  (2hetarange) with a step size of  $0.026^{\circ}$  (measurement time per step, 500 s) at ambient temperature. Raman spectra (Bruker RFS100 FT-Raman) of all NBS glass samples were recorded in the range of  $250-1000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ , in which the samples were excited by an infrared (IR) laser (Nd:YAG) of power 350 mW operating at the wavelength of 1064 nm.

MAS-NMR spectra were recorded for samples NBS-0, NBS-20, and NBS-30 using a Bruker Avance III HD 700 MHz narrow-bore spectrometer. A 4 mm triple-resonance MAS probe was selected at 185.20 MHz (<sup>23</sup>Na) and 224.63 MHz (<sup>11</sup>B) Larmor frequencies. The glasses were spun in ZrO<sub>2</sub> rotors at a rate of 15 kHz. <sup>23</sup>Na MAS-NMR spectra were recorded with a 15° excitation pulse corresponding to 0.35  $\mu$ s and a recycle delay of 2 s. <sup>11</sup>B MAS-NMR spectra were recorded using a Hahn echo experiment with a 90° excitation soft pulse of 6.25  $\mu$ s and a recycle delay of 2 s. The chemical shifts are quoted in parts per million (ppm) using the following secondary references: saturated aqueous solution of NaCl (0 ppm) and 0.1 M aqueous solution of H<sub>3</sub>BO<sub>3</sub> (19.6 ppm) for <sup>23</sup>Na and <sup>11</sup>B, respectively. The obtained MAS-NMR spectra were deconvoluted using the DMFit software.<sup>32</sup>

# 3. RESULTS

**3.1. Physical and Optical Properties.** The XRD patterns of the as-prepared NBS glasses are shown in Figure 1, and the data clearly reveal the amorphous nature. The density ( $\rho$ ) and molar volume ( $V_{\rm m}$ ) are the basic parameters to investigate the structural changes in the glass network since they are strongly influenced by structural compactness or softness, cross-linking, coordination number, etc. Therefore, the physical parameters,



Figure 1. XRD profiles of the NBS glasses.

such as density and molar volume along with electronic polarizability, molar refractivity, etc., have been evaluated for all of the glasses by using the expressions mentioned elsewhere<sup>28</sup> and are presented in Table 1. Figure 2 depicts the variation of density and molar volume of the bulk glasses due to the incorporation of Sb<sub>2</sub>O<sub>3</sub>. From Figure 2, it can be noted that both the density and molar volume of the bulk glasses increase with increasing Sb<sub>2</sub>O<sub>3</sub> content. The enhancement in the density of the NBS glasses is attributed to the replacement of the greater-molecular-mass Sb<sub>2</sub>O<sub>3</sub> (291.52 amu) with the lower-molecular-mass  $B_2O_3$  (69.62 amu) in the glass composition. The increase in molar volume can be attributed to larger ionic size of Sb<sup>3+</sup> (76 pm) ions compared to that of  $B^{3+}$  (23 pm). The values of  $\rho$  and  $V_m$  were found to be in the ranges of 2.281-3.426 g cm<sup>-3</sup> and 29.850-35.576cm<sup>3</sup> mol<sup>-1</sup>, respectively. A similar behavior was also observed with the substitution of Bi<sub>2</sub>O<sub>3</sub> for B<sub>2</sub>O<sub>3</sub> in 15Li<sub>2</sub>O-15K<sub>2</sub>O $xBi_2O_3 - (65 - x)B_2O_3:5V_2O_5$ <sup>33</sup> ZnO $-Bi_2O_3 - B_2O_3$ <sup>34</sup> and boron-silicon-bismuthate<sup>35</sup> glass systems. The atomic packing density  $(C_g)$  values of all of the glasses were calculated using the relation mentioned in ref 36 and are presented in Table 1. It is evident that the  $C_{\rm g}$  values decrease as a function of  $Sb_2O_3$  content. The inset of Figure 2 shows the variation in refractive index (n) with the composition, from which it is evident that n monotonically increases with increasing antimony content in the glasses. Figure 3 presents the UVvis absorption spectra of all of the glass samples. Prepared antimony-containing sodium borate glasses are optically transparent and exhibit good transparency window for wavelengths longer than 400 nm. The glasses turn colorless to pale yellow as antimony content increases in the base glass. Figure 3 illustrates that the UV absorption edge shifted toward the longer wavelengths (red shift) with successive substitution of Sb<sub>2</sub>O<sub>3</sub> for B<sub>2</sub>O<sub>3</sub>.

The optical absorption edge in the UV region is generally utilized to understand the electronic band structure and optical transitions in a material. In general, there are two kinds of optical transitions, namely, direct and indirect transitions, which can be estimated using fundamental absorption edge of linear absorption spectra of the material. Figure 4a,b presents the plots of  $(\alpha h\nu)^2$  versus  $h\nu$  and  $(\alpha \bar{h}\nu)^{1/2}$  versus  $h\nu$ , respectively, where " $\alpha$ " is the absorption coefficient given by  $\alpha(\lambda) = 2.303\left(\frac{A}{t}\right), h$  is Plank's constant, "A" is the energyindependent constant related to band tailing parameter, and " $\nu$ " is the frequency of photon. These plots are utilized to estimate the energy gaps of direct  $(E_g^{\text{ dir}})$  and indirect  $(E_g^{\text{ indir}})$ allowed transitions according to the procedure mentioned elsewhere.<sup>37–39</sup> The energy gap values of direct  $(E_g^{\text{dir}})$  and indirect  $(E_g^{\text{indir}})$  transitions are calculated by extrapolating the linear portions of the plots to reach  $(\alpha h\nu)^2 = 0$  and  $(\alpha h\nu)^{1/2} =$ 0 as shown in Figure 4a,b, respectively. The calculated direct and indirect optical band gap energies  $(E_g^{\text{dir}} \text{ and } E_g^{\text{indir}})$ , respectively) of NBS glass samples are tabulated in Table 1, and the values are in the ranges of  $3.99-3.25 \text{ eV} (\pm 0.02 \text{ eV})$ for  $E_g^{\text{dir}}$  and 3.26–2.78 eV ( $\pm 0.02$  eV) for  $E_{\sigma}^{\text{indir}}$ .

**3.2. Raman Spectroscopy.** Raman spectroscopy is one of the effective and often utilized tools to identify structural groups, environment, and dynamics of vitreous materials. Structural modifications with replacement of  $B_2O_3$  by  $Sb_2O_3$  were evaluated by collecting the Raman spectra for all of the bulk glass samples and are presented in Figure 5. The Raman

Table 1. Physical and Optical Properties of 20Na<sub>2</sub>O-(80 - x)B<sub>2</sub>O<sub>3</sub>-xSb<sub>2</sub>O<sub>3</sub>

glasses	NBS-0	NBS-10	NBS-20	NBS-30
physical properties				
avg. molecular weight, $M$ (g mol <sup>-1</sup> )	68.09	90.28	112.47	134.66
density, $ ho  ({ m g}  { m cm}^{-3})  (\pm 0.002)$	2.281	2.822	3.028	3.426
atomic packing density, $C_{\rm g}$ (±0.002)	0.634	0.603	0.525	0.501
molar volume, $V_{\rm m} ~({\rm cm}^3 ~{\rm mol}^{-1}) ~(\pm 0.002)$	29.850	31.888	33.708	35.576
refractive index, $n \ (\pm 0.001)$	1.512	1.684	1.746	1.854
dielectric constant, $\varepsilon$ (±0.001)	2.286	2.835	3.048	3.437
molar refractivity, $R_{\rm M}~({\rm cm}^{-3})~(\pm 0.002)$	8.927	12.050	13.594	15.894
electronic polarizability, $\alpha_{\rm e}~(\times 10^{-24}~{\rm cm^3})~(\pm 0.002)$	3.538	4.776	5.388	6.299
optical properties				
direct optical band gap, $E_{\rm g}^{\rm dir}$ (eV) (±0.02)	3.99	3.76	3.49	3.25
indirect optical band gap, $E_{ m g}^{ m indir}$ (eV) (±0.02)	3.26	3.49	3.00	2.78
Urbach energy, $U_{\rm E}~(\pm 0.02)$	0.36	0.38	0.41	0.47



**Figure 2.** Composition dependence of density and molar volume in  $20Na_2O-(80 - x)B_2O_3-xSb_2O_3$  glasses; the inset shows the variation of refractive index as a function of  $Sb_2O_3$  content in the glasses.



Figure 3. UV-vis absorption spectra of all NBS glass samples; the vertical lines inside the figure represent the wavelengths selected for NLO measurements.



**Figure 4.** Tauc's plots used for the measurement of optical band gaps in NBS glasses: (a) direct band gap and (b) indirect band gap.

spectra presented were processed for baseline correction according to the procedure mentioned in ref 40.



**Figure 5.** Compositional dependence of Raman spectra of  $20Na_2O-(80 - x)B_2O_3-xSb_2O_3$  glasses.

3.2.1. Raman Spectra of NBS-0 Glass. Pure vitreous B<sub>2</sub>O<sub>2</sub> glass consists of boroxol rings along with some isolated BO3 units that are not part of boroxol ring. The presence of boroxol rings results in a vibration band at around 800 cm<sup>-1</sup> in the Raman spectrum. It has been reported<sup>41</sup> that the intensity of this band substantially decreases with increasing alkali metal cation concentration due to the conversion of the boroxol ring into BO<sub>4</sub>-containing six-membered rings (tetraborate, pentaborate, and triborategroups). The process of this conversion can be recognized with the development of the Raman vibrational band near 770 cm<sup>-1</sup>. This results in the formation of a complex network involving boroxol rings coupled with fourfold-coordinated boron in alkali borate glasses.<sup>42</sup> The development of strong Raman band at 772 cm<sup>-1</sup> as well as a shoulder at 802 cm<sup>-1</sup> in NBS-0 glass evidences the formation of such complex networks. The band appearing at 802 cm<sup>-1</sup> is indicative of breathing vibrations of boroxol rings,43 and the band at 772 cm<sup>-1</sup> confirms that sodium ions favor the formation of BO<sub>4</sub>-containing six-membered rings (tetraborate, pentaborate, and triborategroups) at the expense of boroxol rings.<sup>44</sup> The identification of specific structural group is also possible with the recognition of other associated vibrational bands present in the Raman spectrum. The simultaneous existence of bands at 930, 770, 640, and 480  $\rm cm^{-1}$  in the

Raman spectra of NBS-0 glass clearly indicates that the pentaborate anionic groups  $[(B_5O_{10})^{5-}]$  are present in the glass structure.<sup>45</sup> The presence of pentaborate groups in similar alkali borate glass compositions has also been reported.<sup>41–43</sup> Based on these findings, the peak observed at 772 cm<sup>-1</sup> is unambiguously assigned to the pentaborate groups. The observed band at 920 cm<sup>-1</sup> is attributed to the vibration of planar orthoborate units.<sup>46</sup>

3.2.2. Raman Spectra of Antimony-Containing Glasses. The addition of antimony to the binary sodium borate glasses significantly changed the Raman spectra, indicating several modifications in the network. The band observed at 802 cm<sup>-1</sup> in NBS-0 glass is completely absent in antimony-containing glasses. This clearly suggests that antimony might have entered and disrupted the boroxol rings in the alkali borate glass structure. This type of feature was also reported by Terashima et al.<sup>17</sup> for  $Sb_2O_3-B_2O_3$  binary glasses. Nevertheless, this observation was made only after the addition of 40 mol % of  $Sb_2O_3$ . The Raman spectrum in the range of 200–750 cm<sup>-1</sup> is very broad and is dominated by the Sb<sub>2</sub>O<sub>3</sub> vibrational modes.<sup>47</sup> It has been recently reported that the vitreous antimony materials exhibit a complex Raman spectrum consisting of three broad bands located at 605, 465, and 408 cm<sup>-1,48</sup> The 605 cm<sup>-1</sup> band was assigned to the antisymmetric stretching vibrations of the Sb-O-Sb bridges. The 408 and 465 cm-Raman peaks were ascribed to the symmetric and antisymmetric stretching vibrations of the SbO<sub>2</sub> pyramids, respectively.<sup>48</sup> The presence of peaks observed at 460 cm<sup>-1</sup> in antimony-containing glasses is therefore assigned to the stretching modes of SbO3 units. However, it should be highlighted at this point that the Raman spectrum of antimony-containing glasses is mainly dominated by Sb-O vibrational modes and depressed the B-O vibrational modes in the measured wavenumber range. Therefore, the peaks observed in NBS-10 cannot be readily assigned to specific vibrational bonds, although peaks at 523 and 710 cm<sup>-1</sup> are detectable in NBS-10 glass. The peak that appeared at 772  $cm^{-1}$  is clearly identifiable up to 30 mol % of Sb<sub>2</sub>O<sub>3</sub> addition. This indicates that the antimony-containing borate glasses have large concentration of pentaborate groups. The broadly pronounced Raman band centered at ~650 cm<sup>-1</sup> can be attributed to common vibration of B-O-Sb linkages formed due to the merging of Sb-O-Sb bridges with B-O-B linkages.<sup>49,50</sup> This band is continuously upshifting with further addition of Sb<sub>2</sub>O<sub>3</sub> into the glass composition. From Figure 5, it is also apparent that with increasing Sb<sub>2</sub>O<sub>3</sub> concentration (above 10 mol %), the Raman band observed at ~466  $\text{cm}^{-1}$ shifted to lower values combined with an increase in the intensity.

**3.3. MAS-NMR Spectroscopy.** 3.3.1. <sup>11</sup>B MAS-NMR. <sup>11</sup>B MAS-NMR spectra of NBS glasses with varying concentrations of Sb<sub>2</sub>O<sub>3</sub> are shown in Figure 6a. In borate glasses, boron usually exists in trigonal (B<sup>3</sup>, coordination no: 3) and tetrahedral (B<sup>4</sup>, coordination no: 4) units.<sup>43</sup> <sup>11</sup>B MAS-NMR spectra of glasses show a good resolution of B<sup>3</sup> and B<sup>4</sup> species with two broad peaks centered at ~15 and ~1 ppm, respectively. The relative concentrations of B<sup>3</sup> and B<sup>4</sup> units obtained after deconvolution of <sup>11</sup>B MAS-NMR spectra (Figure 6a) and the corresponding parameters are presented in Table 2. For the good fitting of the spectra, the B<sup>3</sup> peak was fitted with two peaks, namely, B<sup>3(1)</sup> and B<sup>3(II)</sup>, while the B<sup>4</sup> peak was fitted with two peaks for NBS-0 (B<sup>4(I)</sup>). For glass NBS-0, the



Article

Figure 6. MAS-NMR spectra and their deconvolutions using DMFit software of NBS glasses: (a)  $^{11}$ B MAS-NMR spectra and (b)  $^{23}$ Na MAS-NMR spectra of NBS glasses.

Table 2. <sup>11</sup>B MAS-NMR Deconvolution Parameters of NBS Glasses

glass	B <sup>4</sup> (%)	$B^{n(x)}$	$\delta_{ m iso}\( m ppm)$	amount (%)	C <sub>Q</sub> (MHz)	$\eta_{o}$
NBS-0	20.17	B <sup>3(I)</sup>	18.01	69.97	2.62	0.31
		$B^{3(II)}$	15.23	9.86	2.58	0.36
		$B^{4(I)}$	0.60	15.78		
		$B^{4(II)}$	1.75	4.39		
NBS-20	21.75	B <sup>3(I)</sup>	18.31	72.63	2.61	0.26
		$B^{3(II)}$	16.50	5.63	2.08	0.95
		$B^{4(I)}$	1.15	21.75		
NBS-30	24.90	B <sup>3(I)</sup>	18.27	69.81	2.56	0.10
		$B^{3(II)}$	16.16	5.29	2.05	0.98
		$B^{4(I)}$	1.20	24.90		

lines  $B^{3(I)}$  and  $B^{3(II)}$  correspond to ring and nonring  $B^3$  structures.<sup>51–53</sup> In rest of the glass compositions,  $B^{3(I)}$  and  $B^{3(II)}$  correspond to symmetric and asymmetric  $B^3$  units.<sup>51,54</sup> The two lines of  $B^4$  for NBS-0 glass denoted by  $B^{4(I)}$  and  $B^{4(II)}$  might correspond to  $B^4$  units in different configurations such as diborate, triborate, pentaborate, etc.<sup>55</sup> Svenson et al.<sup>43</sup> also reported the presence of two  $B^4$  line shapes for a similar glass composition. With addition of  $Sb_2O_3$ , the fraction of  $B^4$  units increases (Table 2), which would have a positive effect on the glass stability.<sup>56</sup> Nevertheless, Terashima et al.<sup>17</sup> attempted to improve the nonlinear property of borate glasses through limiting the concentration of  $B^4$  units with the addition of  $Sb_2O_3$ . This is achieved owing to the strong covalent character of Sb–O bonds.<sup>17,26,57</sup>

3.3.2. <sup>23</sup>Na MAS-NMR. The <sup>23</sup>Na MAS-NMR spectra and their deconvolution for all glasses are shown in Figure 6b, which display a broad resonance band. <sup>23</sup>Na MAS-NMR parameters after the decomposition are enlisted in Table 3.

# Table 3. <sup>23</sup>Na MAS-NMR Deconvolution Parameters of NBS Glasses

glass	$\delta_{ m iso}~( m ppm)$	$C_{\rm Q}$ (MHz)	$\eta_{o}$
NBS-0	-6.94	2.557	0.86
NBS-20	-3.55	2.324	0.83
NBS-30	-2.58	2.275	0.70

Angeli et al.<sup>58</sup> demonstrated that increasing Na–O bond length decreases the <sup>23</sup>Na MAS-NMR chemical shift toward the lower ppm. It is known that Na–O bond length is longer when sodium acts as a charge compensator than modifier cation. In the current glasses, with increasing  $Sb_2O_3$  content, the <sup>23</sup>Na chemical shift increases.

**3.4. Femtosecond NLO Properties.** The sign and magnitude of nonlinear refraction and absorption coefficients of all glasses were determined by the Z-scan technique. In the present study, we performed nonlinear measurements in OA and CA Z-scan modes for measuring the nonlinear absorption and refraction, respectively, in the spectral range of 750–880 nm with fs pulse excitation. Figure 7a depicts the OA Z-scan



**Figure 7.** Z-scan signatures of NBS glasses: (a) open-aperture Z-scan plots and (b) closed-aperture Z-scan plots. The open circles represent the experimental data, and the solid lines are indicative of theoretically fitted data.

plots of sodium borate glasses with different concentrations of  $Sb_2O_3$  at 750, 800, and 880 nm. The peak intensities in the Z-scan measurements were in the range of  $2 \times 10^8 - 4 \times 10^8$  W cm<sup>-2</sup> for all of the samples and are similar at all of the wavelengths used in the present study. It is to be noted that even with this intensity, the photodarkening effect was not observed in the samples. From Figure 7a, it is evident that OA Z-scan plots demonstrate a dip at focal point. This could be considered as a signature of reverse saturable absorption (RSA) property in the antimony-containing glasses. In general, in OA Z-scan mode, the output transmittance of the laser

beam decreases and becomes minimum at focal point (Z = 0) and hence results a valley at focal point, as shown in Figure 7a. Nevertheless, the observed RSA kind of nonlinearity indicates the simultaneous absorption of two or more photons (i.e., 2PA, 3PA, and so on). To identify the number of photons absorbed for observed nonlinearity, we have considered the general multiphoton absorption (MPA) equation<sup>59</sup>

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

where  $\alpha_n$  is the effective multiphoton absorption coefficient ("*n*" is the order or absorption process, n = 2 for 2PA, n = 3 for 3PA, and etc.),  $I_{00}$  is the peak intensity of the laser beam,  $L_{\text{eff}} = \frac{1 - e^{-(n-1)\alpha_0 L}}{\alpha_0}$  is the effective path length, *Z* is the position of the sample,  $Z_0 = \pi \omega_0^2 / \lambda$  is the Rayleigh range,  $\omega_0$  is the beam waist at Z = 0 (focal point), and  $\lambda$  is the excitation wavelength.

Experimental OA Z-scan data of all of the glasses were best fitted with eq 1 for n = 2, and the obtained  $\alpha_2$  values are provided in Table 4 for different wavelengths. The errors mentioned in the data arise mainly from errors in the estimation of beam waist at focus and the resulting errors in peak intensities along with fitting errors. From Figure 7a, it is evident that the incorporation of Sb<sub>2</sub>O<sub>3</sub> yielded the RSA nonlinearity in the NBS glasses since NBS-0 did not demonstrate any dip at focal point. A similar kind of RSA behavior is also observed in other borate glass systems.<sup>4,5,18,19</sup> Figure 7b illustrates the CA Z-scan curves of antimonycontaining glasses with different concentrations of Sb<sub>2</sub>O<sub>3</sub> at 750, 800, and 880 nm. From Figure 7b, it is clear that the prefocal dip is followed by a postfocal peak, and it is a clear signature for a positive nonlinear refractive index. This positive nonlinear refraction is due to self-focusing effect.<sup>4</sup> The nonlinear refractive index  $(n_2)$  value can be estimated by using the phase difference value  $(\Delta \Phi_0)$  and is given by

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

The phase difference value  $(\Delta \Phi_0)$  is, therefore, obtained by fitting the CA Z-scan experimental data (dotted lines in Figure 7b) using eq 3 (solid lines in Figure 7b).<sup>4,60</sup>

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

where  $\Delta \Phi_0$  is the phase difference of the laser beam caused due to nonlinear refraction. The obtained  $n_2$  values of NBS glasses are reported in Table 4. Similar positive nonlinear

Table 4. Summary of NLO Coefficients of NBS Glasses Obtained from the fs Z-Scan Experiments

glass	$\lambda$ (nm)	$\alpha ~({\rm cm}^{-1})$	$\alpha_2 \ (cm(GW)^{-1})$	$n_2 (\times 10^{-18} \text{ m}^2 \text{ W}^{-1})$	$\operatorname{Re}\chi^{(3)}$ (×10 <sup>-13</sup> esu)	$\text{Im}\chi^{(3)}~(\times 10^{-13}~\text{esu})$	$\chi^{(3)}$ (×10 <sup>-13</sup> esu)
NBS-10	750	10.69	$0.21 (\pm 0.02)$	0.38 (±0.05)	2.73	0.90	2.87
	800	10.63	0.14 (±0.01)	0.21 (±0.03)	1.51	0.64	1.64
	880	10.48	$0.07 (\pm 0.001)$	$0.16 (\pm 0.02)$	1.15	0.35	1.2
NBS-20	750	14.38	0.57 (±0.05)	$0.62 (\pm 0.09)$	4.79	2.63	5.46
	800	14.25	$0.46 (\pm 0.04)$	0.51 (±0.07)	3.94	2.26	4.54
	880	14.18	0.39 (±0.03)	$0.47 (\pm 0.07)$	3.63	2.11	4.19
NBS-30	750	20.14	$0.88 (\pm 0.08)$	1.04 (±0.15)	9.06	4.58	10.1
	800	19.95	$0.82 (\pm 0.08)$	0.87 (±0.13)	7.58	4.55	8.83
	880	19.85	$0.74 (\pm 0.07)$	$0.72 (\pm 0.10)$	6.27	4.51	7.72

Та	ble	5.	NL	0	Coefficients	of	Some	Selected	Glass	Compositions
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glass composition	wavelength and pulse sizes	two-photon absorption coefficients $(\alpha_2, \ { m cm}({ m GW})^{-1})$	nonlinear refractive index $(n_2, m^2 W^{-1})$	reference
10CaO-35Bi <sub>2</sub> O <sub>3</sub> -55B <sub>2</sub> O <sub>3</sub>	800 nm (100 fs)	$2.8 \times 10^{-2}$		19
	532 nm (30 ps)	1.3		19
	532 nm (6 ns)		$1.6 \times 10^{-16}$	19
10SrO-35Bi <sub>2</sub> O <sub>3</sub> -55B <sub>2</sub> O <sub>3</sub>	800 nm (100 fs)	$3.4 \times 10^{-2}$		19
	532 nm (30 ps)	2.4		19
	532 nm (6 ns)		$3.2 \times 10^{-16}$	19
$10BaO - 35Bi_2O_3 - 55B_2O_3$	532 nm (6 ns)		$4.7 \times 10^{-16}$	19
$45Bi_2O_3 - 3ZnO - 25B_2O_3$	800 nm (110 fs)	1.04	$1.5 \times 10^{-19}$	4
	532 nm (30 ps)	24.6		4
fused silica	1064 nm		$2.7 \times 10^{-20}$	62
	355 nm	$1.25 \times 10^{-3}$	$2.5 \times 10^{-20}$	62
BK-10 (borosilicate crown glass)	1064 nm		$2.8 \times 10^{-20}$	62
	355 nm	0.0055	$1.7 \times 10^{-20}$	62
25Bi <sub>2</sub> O <sub>3</sub> -37.5ZnO-37.5B <sub>2</sub> O <sub>3</sub>	1064 nm (100 ps)	<0.02	$1 \times 10^{-18}$	63
	800 nm (150 fs)	<0.01	$2.9 \times 10^{-19}$	63
	532 nm (80 ps)	5.5	$3 \times 10^{-18}$	63
12.5Bi <sub>2</sub> O <sub>3</sub> -43.5ZnO-43.5B <sub>2</sub> O <sub>3</sub>	1064 nm (100 ps)	<0.02	$<5 \times 10^{-19}$	63
	800 nm (150 fs)	<0.01	$1.3 \times 10^{-19}$	63
	532 nm (80 ps)	1.5	$1.8 \times 10^{-18}$	63

refraction results are also observed for other borate glass system.<sup>4,5,61</sup> Similar to 2PA ( $\alpha_2$ ) coefficient, the  $n_2$  values also increased with the addition of Sb<sub>2</sub>O<sub>3</sub>, and a highest value was observed for the NBS-30 glass. All of the values of  $\alpha_2$  and  $n_2$  at different excitation wavelengths for all NBS glasses are enlisted in Table 4. It is observed that the  $\alpha_2$  and  $n_2$  increased with increasing antimony contents in NBS glasses or, in other words, both the  $\alpha_2$  and  $n_2$  increase with decreasing energy gap. From Table 4, it is also evident that both ( $\alpha_2$  and  $n_2$ ) show monotonous increase as the energy of excitation wavelength approaches the energy gap, and this effect known as resonance enhancement of nonlinearity usually occurs when the frequency (energy) of excited laser radiation approaches the linear absorption of the material.<sup>5</sup> Further, the  $\alpha_2$  and  $n_2$  values of the selected glass compositions are enlisted in Table 5.<sup>4,19,62,63</sup> The intensity-dependent NLO properties were measured using OA Z-scan mode at three spectral regions for NBS-20 and NBS-30 glasses. The variation of  $\alpha_2$  with respect to input intensities is shown in Figure 8, and it is evident that the changes were within the experimental error suggesting the absence of other types of nonlinearities (highorder or excited-state absorption induced).

	1.0 -	
	0.0	NBS-30 @ 750 nm
	0.9-	NBS-30 @ 800 nm
	0.8 -	NBS-30 @ 880 nm
(GW)	0.7 –	NBS-20 @ 750 nm
сШ	0.6 -	• • •
$\alpha_2($	0.5 -	NBS-20 @ 800 nm
		NBS-20 @ 880 nm
	0.4 –	•
	2	2.2 2.4 2.6 2.8 3.0 3.2
	1	nput Intensity (x 10° W cm <sup>-2</sup> )

**Figure 8.** Intensity dependence of two-photon absorption coeffcient  $(\alpha_2)$  of NBS-20 and NBS-30 glasses.

The real and imaginary parts of  $\chi^{(3)}$  can be evaluated using the following equations<sup>64</sup>

$$\operatorname{Re} \chi^{(3)}(\operatorname{esu}) = \frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2(\mathrm{m}^2/\mathrm{W})$$
(4)

$$\operatorname{Im} \chi^{(3)}(\operatorname{esu}) = \frac{\lambda \varepsilon_0 c^2 n_0^2}{4\pi^2} \alpha_2(\mathrm{m/W})$$
(5)

where c,  $\varepsilon_0$ , and  $n_0$  are the velocity of light, permittivity of vacuum, and linear refractive index of the glass, respectively. The total  $\chi^{(3)}$  can be evaluated using the relation

$$|\chi^{(3)}|(\text{esu}) = \{(\text{Re}\,\chi^{(3)})^2 + (\text{Im}\,\chi^{(3)})^2\}^{1/2}$$
(6)

All of the evaluated real and imaginary nonlinear susceptibility values along with the total nonlinear susceptibility ones are also presented in Table 4. It is clear that the obtained  $\chi^{(3)}$ values of the present NBS glasses are 1 order of magnitude greater than those of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary glasses.<sup>17</sup> Further, Lin et al.<sup>65</sup> measured the nonlinear response time of  $Bi_2O_3$ -B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses via optical Kerr shutter experiment at 800 nm and by utilizing 30 fs pulses at a repetition rate of 1 kHz, and the estimated response time was <90 fs. Sugimoto et al.<sup>66</sup> studied the temporal dynamics of glasses consisting of Bi<sub>2</sub>O<sub>3</sub> through degenerate four-wave mixing method at 810 nm using 200 fs laser pulses and found that the studied glasses show electronic response below 200 fs. Similarly, Yu et al.<sup>67</sup> evaluated the optical nonlinearity of HMO glasses through the optical Kerr gate method and found that the temporal response was faster than 350 fs. Falcão-Filho et al.<sup>27</sup> measured the response time of antimony orthophosphate glasses, in which the correlation signals between pump and probe pulses represent ultrafast response (<100 fs) for all glass compositions. Their results clearly demonstrated 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 pulse. In the present investigation, the optical nonlinearity was obtained with 150 fs, 80 MHz repetition rate laser pulses, and this signifies that the nonlinearity has a

femtosecond (ultrafast) component, and due to high repetition rate (and small absorption at the excited wavelengths), there could be thermal component also.

#### 4. DISCUSSION

4.1. Glass Structure. The addition of modifier oxide to the  $B_2O_3$  system initially converts the  $B^3$  (boroxol rings) units into B<sup>4</sup> units, and the formation of NBOs initiates only at higher modifier concentrations. For the well-known sodium borate system, it is postulated that the addition of sodium results in the formation of NBOs only for R ( $R = R_2O/B_2O_3$ , where  $R_2O$ is the alkali oxide) greater than 0.5. For  $R \leq 0.5$ , all of the alkali cations act only as charge compensators. It is therefore expected that the presence of NBOs in NBS-0 glass (R = 0.25) should be zero. The Raman spectrum for NBS-0 glass clearly indicates the presence of pentaborate groups consisting of BO<sub>3</sub> units and BO4 units. Nevertheless, the Raman spectrum does not reveal the presence of NBO-containing borate units in NBS-0 glass. The NMR spectrum, however, provides the experimental fraction of  $B^4$  units (~0.20) that is slightly below the R (0.25) value. This indicates that small concentrations of Na cations are also involved in the formation of NBOs, which could not be determined due to the broad B<sup>3</sup> peak. The concentration of NBOs calculated based on the equation mentioned elsewhere<sup>68</sup> assuming that all NBOs are associated with BO3 sites showed nearly 3% of oxygens present as NBO in NBS-0 glass. Further, the appearance of a small intense Raman peak at 920 cm<sup>-1</sup> also indicates the presence of a small fraction of isolated BO<sub>3</sub><sup>3-</sup> boron units in NBS-0 glass.

The addition of  $\text{Sb}_2\text{O}_3$  to NBS-0 glass slightly increased the fraction of B<sup>4</sup> units. This cannot be attributed to the variation of Na/B ratio with the addition of  $\text{Sb}_2\text{O}_3$ . If this was the case, the expected amounts of B<sup>4</sup> units should be ~25, 33, and 40% for NBS-0, NBS-20, and NBS-30, respectively. However, this is not in agreement with the experimental values (Table 2). Therefore, the structural changes upon the addition of  $\text{Sb}_2\text{O}_3$  are complex.

The structures of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass have been considered to be SbO3 trigonal pyramid. Nevertheless, Masuda et al.,69 using X-ray fluorescence, found that Sb<sup>3+</sup> (in trigonal pyramids) and Sb<sup>5+</sup> (in octahedral form) were both present in nearly equal amounts in binary alkali and alkaline earth antimonite glasses. It is interesting to note that the BO<sub>4</sub> units, even though their fractions are very small, were also found in the  $Sb_2O_3-B_2O_3$  glass system as in the  $Bi_2O_3-B_2O_3$  system.<sup>17</sup> On the other hand,  $BO_4$  units were not found in  $GeO_2-B_2O_3$ glasses for the GeO2 ranges from 15 to 100 mol %.<sup>17</sup> This clearly indicates that the Sb cations play the role of charge compensator in Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass system. However, the type of charge compensating species in Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass is not yet clear. It has been reported that small part of Sb<sub>2</sub>O<sub>3</sub> transforms into Sb<sub>2</sub>O<sub>5</sub> during the melting process owing to the interaction with oxygen in air.<sup>70</sup> Sb<sub>2</sub>O<sub>5</sub> consists of distorted corner- and edge-sharing Sb<sup>5+</sup>O<sub>6</sub> octahedra.<sup>71-73</sup> Masuda et al.<sup>69</sup> concluded that both Sb<sup>3+</sup> and Sb<sup>5+</sup> were present in nearly equal amounts in the binary alkali and alkaline earth antimonite glasses. Holland et al.<sup>26</sup> further confirmed the presence of Sb<sup>5+</sup> and Sb<sup>3+</sup> in binary Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses through Mossbauer spectroscopy. It was also identified that the percentage of Sb<sup>5+</sup> cations increased with monotonic increase of Sb<sub>2</sub>O<sub>3</sub>. Therefore, the charge compensation for the formation of  $[BO_4]^-$  is only due to the presence of  $Sb^{5+}O_6$  octahedra.<sup>26</sup> The <sup>23</sup>Na MAS-NMR chemical shift is oppositely related to the Na-O

bond length and/or coordination number. It decreases with the increasing average Na–O bond length. The increasing percentage of Na as charge compensators results in larger Na– O distances and thus decreases the chemical shift. In the current glasses, the increase in sodium chemical shift (Figure 6b and Table 3) with increase in Sb<sub>2</sub>O<sub>3</sub> indicates the role of sodium as charge compensator decreases. This is substantiated by the occurrence of asymmetric B<sup>3</sup> units in the antimonycontaining glasses (Figure 6a and Table 2). The change in Na cation's role from charge compensation to NBOs resulted in the formation of asymmetric B<sup>3</sup> units. Further, Raman spectra (Figure 5) also show decrease in the three-membered boroxol rings with the addition of Sb<sub>2</sub>O<sub>3</sub>.

It is known that the  $Sb_2O_3$  is a conditional glass former and it forms the glass in the presence of modifiers or other glass formers (like  $B_2O_3/P_2O_5/TeO_2/GeO_2$ ). The triangular SbO<sub>3</sub> pyramids with the three oxygen atoms at corners (Sb–O bond lengths as 0.2023, 0.2019, and 0.1977 nm) and the lone pair of electrons at the fourth corner are the main building blocks in the antimony glass.<sup>50</sup> The presence of 650 cm<sup>-1</sup> band in Raman spectrum indicates that the third oxygen in each SbO<sub>3</sub> units is linked with boron units and formed the Sb–O–B linkages.<sup>74</sup> The similarity between the electronegativities of boron (2.0) and antimony (1.9) is also responsible for the formation of such Sb–O–B linkages in antimony borate glasses.<sup>26</sup>

**4.2.** Structure–Physical Properties. The substitution of antimony for boron in the parent glass has a significant effect on the structure and properties of glass. The density and molar volume of NBS glasses increase with Sb<sub>2</sub>O<sub>3</sub>. Nevertheless, the atomic packing density decreases with increase in Sb<sub>2</sub>O<sub>3</sub> in the composition. The increase in density with incorporation of  $Sb_2O_3$  for  $B_2O_3$  in the glass composition is a predictable result since  $Sb_2O_3$  has greater molecular mass compared to  $B_2O_3$ . The enhancement in molar volume of the glasses with respect to Sb<sub>2</sub>O<sub>3</sub> content is attributed to the slight increase in the percentage of oxygen atoms due to  $Sb^{3+} \rightarrow Sb^{5+}$  reaction and larger Sb ionic radii compared to boron (O<sup>2-</sup>: 140 pm, Sb<sup>3+</sup>: 76 pm, Sb<sup>5+</sup>: 60 pm, Na<sup>+</sup>: 102 pm, and B<sup>3+</sup>: 23 pm).<sup>75</sup> The atomic packing density values showed decreasing trend with increasing Sb<sub>2</sub>O<sub>3</sub> content, which is in accordance with molar volume trend. Thus, atomic density and molar volume are inversely related.

4.3. Structure-Optical Properties. It has been reported that the presence of large and polarizable ions increases the NLO properties of the glasses. This is possibly attributed to the large electronic hyperpolarizability character of NBOs compared to bridging oxygens.<sup>76</sup> The decrease in optical band gap with the addition of Sb<sub>2</sub>O<sub>3</sub> suggests that the content of NBOs is increased in the glass matrix.<sup>11</sup> The <sup>23</sup>Na MAS-NMR chemical shift, which shifts toward higher ppm, also indicates that the role of Na as a charge compensator decreases. This supports the increasing role of Na<sup>+</sup> cation as a modifier, which generally converts the bridging oxygen into the NBO, in glass matrix. Franco et al.<sup>47</sup> investigated the influence of Sb<sub>2</sub>O<sub>3</sub> on the plasmonic properties of copper nanoparticles and explained that during the melting process in the temperature range of 500-800 °C, the Sb undergoes a phase transition through oxidation of Sb species, resulting in  $Sb^{5+}$  from  $Sb^{3+}$  (i.e.,  $Sb^{3+} \rightarrow Sb^{5+} + 2e^{-}$ ). Nonetheless, these lone pair of electrons  $(5s^2)$  of  $Sb^{3+}$  cause a high polarization of the O<sup>2-</sup> anion and increase the total electronic polarizability.<sup>29</sup> Further, the Sb atoms having five valence electrons in the outer

electronic shell undergo distortion in the presence of an applied optical field. Thus, large charge displacement can occur, resulting in the greater polarizability of Sb<sup>5+</sup> ion.<sup>77</sup> Such significant displacements produce anharmonic effects, resulting in large cubic hyperpolarizabilities.<sup>78</sup> Interestingly, in oxide glasses, the molar refraction mainly depends on O<sup>2-</sup> ions, and this molar refraction is in turn directly related to  $\chi^{(3)}$  66 Moreover, it is known that the  $O^{2-}$  ions are affected by surrounding cations. The neighboring cations with large ionic radii enlarge the molar refraction of glasses because the ion refraction of the cation itself increases and the asymmetry of the electric field around the  $O^{2-}$  ions becomes larger. The antimony ions have coordination numbers of 5 and 3 in NBS glasses, and their ionic radii are large compared to that of boron. Therefore, the present NBS glasses containing Sb<sub>2</sub>O<sub>3</sub> exhibit large molar refraction.<sup>66</sup> Therefore, the enhancement in NLO coefficients with respect to Sb<sub>2</sub>O<sub>3</sub> can be attributed to the hyperpolarizability of Sb<sup>3+</sup> and Sb<sup>5+</sup> ions. Further, the <sup>11</sup>B MAS-NMR studies, band gap analysis, and the physical properties of the present glasses also clearly evidence the increase of NBOs with gradual substitution of B<sub>2</sub>O<sub>3</sub> by Sb<sub>2</sub>O<sub>3</sub>; hence, it can be concluded that the NBOs also contributed to observed NLO coefficients. The N4 values of present NBS glasses estimated using <sup>11</sup>B MAS-NMR are greater than those of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> binary glasses. This indicates that the formation of NBO due to donation of oxygen of metal oxide to BO3 is greater in the studied glasses compared to binary Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glasses.<sup>17,26</sup> From the data presented in Table 4, one can note that larger variation of  $n_2$  than  $\alpha_2$  as a function of Sb<sub>2</sub>O<sub>3</sub> implies that, possibly, the nonlinear index of refraction  $(n_2)$  is more sensible to Sb<sub>2</sub>O<sub>3</sub> content than the two-photon absorption coefficient ( $\alpha_2$ ).

The increase in nonlinear refractive index  $(n_2)$  is also attributed to the greater Sb–O average bond lengths according to eq 7<sup>79</sup>

$$n_2 = \frac{2.5 \times 10^{-12} f_{\rm L}^3 (n^2 - 1) d^2 E_{\rm s}^6}{n (E_{\rm s}^2 - E^2)^4} (\text{esu})$$
(7)

where  $F_L$  is the Lorentz field factor, *n* is the 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 present glasses, the three bonds are Na–O, B–O, and Sb–O, but the <sup>23</sup>Na MAS-NMR shows that the Na–O bond length decreases upon incorporating Sb<sub>2</sub>O<sub>3</sub>. The Raman spectral measurements showed that the shorter B–O and B–O–B bonds are replaced by Sb–O, Sb–O–Sb, and Sb–O–B bonds upon substituting Sb<sub>2</sub>O<sub>3</sub> for B<sub>2</sub>O<sub>3</sub>. Hence, the concentration of elongated Sb–O bonds is greater in comparison to the shorter B–O bonds per unit volume. Therefore, the increase in  $n_2$  as a function of Sb<sub>2</sub>O<sub>3</sub> can possibly be attributed to the elongated Sb–O bond lengths.

Furthermore, the observed nonlinearity in NBS glasses can also be explained by considering the average bond lengths. Hashimoto et al.<sup>80</sup> explained that the glasses with transitionmetal oxides showed the highest  $\chi^{(3)}$  with the shortest average bond lengths, whereas the glasses with non-transition-metal oxides (e.g., HMOs) exhibited the greatest  $\chi^{(3)}$  due to the longest average bond lengths. In glass network, the Sb–O and B–O bond lengths are reported in the ranges of 2.0–2.6<sup>50</sup> and 1.37–1.48 Å,<sup>81</sup> respectively, and the Sb–O bond concentrations are increasing due to the incorporation of Sb<sub>2</sub>O<sub>3</sub> in the composition; hence, the average bond lengths in the present NBS glasses are greater than B–O bond lengths. Therefore, the enhancement in  $\chi^{(3)}$  is also attributed to large average Sb–O bond lengths. The sodium NMR clearly indicates the shortening of the Na–O bond lengths upon the substitution of Sb<sub>2</sub>O<sub>3</sub> for B<sub>2</sub>O<sub>3</sub> in the glass composition; hence, the influence Na–O average bond lengths can be ignored.

On the application side, to propose the glasses for nonlinear device applications figure of merit is a distinct criterion and is given by  $^{60}$ 

$$F = \frac{2\alpha_2 \lambda}{n_2} \tag{8}$$

where *F* is the figure of merit,  $\alpha_2$  is the two-photon absorption coefficient,  $\lambda$  is the excitation wavelength, and  $n_2$  is the nonlinear refractive index. When the condition F < 1 is satisfied, the glasses could be used for switching applications such as passive mode locking and optical Q-switching of lasers (to produce ultrashort pulses). However, if F > 1 is satisfied, then the glasses could be used for nonlinear limiting applications such as to protect the human eyes and optical sensors from high-fluence irradiation, etc. In the present investigation, the studied glasses possess F > 1 and, therefore, antimony-containing NBS glasses have potential as ultrafast optical limiters.

#### 5. CONCLUSIONS

In summary, the physical, optical, structural, and third-order NLO studies were performed and analyzed to understand the influence of antimony on the structure and optical properties of sodium borate glass system and also to evaluate their suitability for NLO applications. The studied glasses possess good optical transparency and high linear refractive index. The decrease in optical band gap as a function of  $Sb_2O_3$  and the <sup>11</sup>B MAS-NMR studies clearly evidence the enhancement of NBO content in the glasses due to the incorporation of antimony. The Raman scattering results confirmed the formation of B-O-Sb and Sb-O-Sb bands in antimony-containing glasses. <sup>11</sup>B MAS-NMR results disclosed that the N<sub>4</sub> is linearly increased with gradual substitution of Sb<sub>2</sub>O<sub>3</sub> for B<sub>2</sub>O<sub>3</sub> due to the oxidation process of Sb<sup>3+</sup>. The fs NLO measurements confirmed that the  $\alpha_2$  and  $n_2$  values showed an increasing trend as a function of Sb<sub>2</sub>O<sub>3</sub>, which is ascribed to the hyperpolarizability of Sb<sup>3+</sup> and Sb<sup>5+</sup> and also due to the enhanced NBO content. Furthermore, the figure of merit of all investigated antimony-containing NBS glasses revealed that they are potential materials for optical limiting applications.

#### AUTHOR INFORMATION

#### **Corresponding Authors**

\*E-mail: eraiah@rediffmail.com (B.E).

- \*E-mail: jmf@ua.pt (J.M.F.F.).
- \*E-mail: aareddy@cgcri.res.in (A.R.A).

# ORCID 💿

K. Jayanthi: 0000-0002-5016-3575

José M. F. Ferreira: 0000-0002-7520-2809 Amarnath R. Allu: 0000-0003-0450-0929

#### **Author Contributions**

<sup>#</sup>G.J. and A.G. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Singh, S. P.; Karmakar, B. Photoluminescence Enhancement of  $Eu^{3+}$  by Energy Transfer from  $Bi^{2+}$  to  $Eu^{3+}$  in Bismuth Glass Nanocomposites. *RSC Adv.* **2011**, *1*, 751–754.

(2) Mancuso, E.; Bretcanu, O.; Marshall, M.; Dalgarno, K. W. Sensitivity of Novel Silicate and Borate-Based Glass Structures on in Vitro Bioactivity and Degradation Behaviour. *Ceram. Int.* **2017**, *43*, 12651–12657.

(3) Islam, M. T.; Felfel, R. M.; Neel, E. A. A.; Grant, D. M.; Ahmed, I.; Hossain, K. M. Z. Bioactive Calcium Phosphate-Based Glasses and Ceramics and Their Biomedical Applications: A Review. *J. Tissue Eng.* **2017**, *8*, No. 2041731417719170.

(4) Shanmugavelu, B.; Kumar, V. V. R. K.; Kuladeep, R.; Rao, D. R. Third Order Nonlinear Optical Properties of Bismuth Zinc Borate Glasses. J. Appl. Phys. 2013, 114, No. 243103.

(5) Almeida, J. M. P.; De Boni, L.; Hernandes, A. C.; Mendonça, C. R. Third-Order Nonlinear Spectra and Optical Limiting of Lead Oxifluoroborate Glasses. *Opt. Express* **2011**, *19*, 17220–17225.

(6) Hivrekar, M. M.; Sable, D. B.; Solunke, M. B.; Jadhav, K. M. Different Property Studies with Network Improvement of CdO Doped Alkali Borate Glass. J. Non-Cryst. Solids **2018**, 491, 14–23.

(7) Chen, C.; Wu, Y.; Li, R. The Anionic Group Theory of the Non-Linear Optical Effect and Its Applications in the Development of New High-Quality NLO Crystals in the Borate Series. *Int. Rev. Phys. Chem.* **1989**, *8*, 65–91.

(8) Zhang, W.; Yu, H.; Wu, H.; Halasyamani, S. P. Crystal Growth and Associated Properties of a Nonlinear Optical Crystal—Ba<sub>2</sub>Zn-(BO<sub>3</sub>)<sub>2</sub>. *Crystals* **2016**, *6*, No. 68.

(9) Luo, M.; Song, Y.; Liang, F.; Ye, N.; Lin, Z. Pb<sub>2</sub>BO<sub>3</sub>Br: A Novel Nonlinear Optical Lead Borate Bromine with a KBBF-Type Structure Exhibiting Strong Nonlinear Optical Response. *Inorg. Chem. Front.* **2018**, *5*, 916–921.

(10) Xue, D.; Betzler, K.; Hesse, H.; Lammers, D. Nonlinear Optical Properties of Borate Crystals. *Solid State Commun.* **2000**, *114*, 21–25.

(11) Rani, S.; Sanghi, S.; Ahlawat, N.; Agarwal, A. Influence of  $Bi_2O_3$  on Thermal, Structural and Dielectric Properties of Lithium Zinc Bismuth Borate Glasses. *J. Alloys Compd.* **2014**, *597*, 110–118.

(12) El-Shishtawi, N. A.; Tawansi, A.; Gohar, I. A.; Holland, D. Some Physical Properties of Lead Borate Glasses. I. Influences of Heat Treatment and PbO Content. J. Phys. D: Appl. Phys. 1988, 21, 607.

 (13) Rada, S.; Culea, E.; Neumann, M. Experimental and Theoretical Studies of the Structure of Tellurate-Borate Glasses Network. J. Mol. Model. 2010, 16, 1333–1338.

(14) Abo-Naf, S. M.; Darwish, H.; El-Desoky, M. M. Properties and Structure of Germanium-Containing Lithium Aluminoborate Glasses. *J. Mater. Sci.: Mater. Electron.* **2002**, *13*, 537–542.

(15) Yazdi, A. R.; Towler, M. The Effect of the Addition of Gallium on the Structure of Zinc Borate Glass with Controlled Gallium Ion Release. *Mater. Des.* **2016**, *92*, 1018–1027.

(16) Singh, G. P.; Singh, D. P. Effect of WO<sub>3</sub> on Structural and Optical Properties of  $CeO_2$ -PbO-B<sub>2</sub>O<sub>3</sub> glasses. *Phys. B* **2011**, 406, 640-644.

(17) Terashima, K.; Hashimoto, T.; Uchino, T.; Kim, S.-H.; Yoko, T. Structure and Nonlinear Optical Properties of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> Binary Glasses. *J. Ceram. Soc. Jpn.* **1996**, *104*, 1008–1014.

(18) Rao, M. V.; Kumar, V. V. R. K.; Shihab, N.; Rao, D. N. Z-Scan Studies of Barium Bismuth Borate Glasses. *Opt. Mater.* **2018**, *84*, 178–183.

(19) Rao, M. V.; Kumar, V. V. R. K.; Shihab, N. K.; Rao, D. N. Third Order Nonlinear and Optical Limiting Properties of Alkaline Bismuth Borate Glasses. *Opt. Laser Technol.* **2018**, *107*, 110–115.

(20) Munoz-Martin, D.; de La Cruz, A. R.; Fernandez-Navarro, J. M.; Domingo, C.; Solis, J.; Gonzalo, J. Structural Origin of the Nonlinear Optical Properties of Lead Niobium Germanate Film Glasses. J. Appl. Phys. 2011, 110, No. 023522.

(21) Som, T.; Karmakar, B. Structure and Properties of Low Phonon Antimony Glasses in the  $K_2O-B_2O_3-Sb_2O_3-ZnO$  System. J. Am. Ceram. Soc. **2009**, 92, 2230–2236.

(22) Qian, Q.; Zhang, Q. Y.; Jiang, H. F.; Yang, Z. M.; Jiang, Z. H. The Spectroscopic Properties of  $Er^{3+}$ -Doped Antimony-borate Glasses. *Phys. B* **2010**, 405, 2220–2225.

(23) Gandhi, Y.; Purnachand, N.; Sudhakar, K. S. V.; Satyanarayana, T.; Veeraiah, N. Influence of Modifier Oxides on Some Physical Properties of Antimony Borate Glass System Doped with  $V_2O_5$ . *Mater. Chem. Phys.* **2010**, *120*, 89–97.

(24) Honma, T.; Benino, Y.; Komatsu, T.; Sato, R.; Dimitrov, V. Structural Relaxation Kinetics of Antimony Borate Glasses with Covalent Bonding Character. J. Chem. Phys. **2001**, 115, 7207–7214.

(25) Nalin, M.; Messaddeq, Y.; Ribeiro, S. J. L.; Poulain, M.; Briois, V.; Brunklaus, G.; Rosenhahn, C.; Mosel, B. D.; Eckert, H. Structural Organization and Thermal Properties of the Sb<sub>2</sub>O<sub>3</sub>–SbPO<sub>4</sub> Glass System. *J. Mater. Chem.* **2004**, *14*, 3398–3405.

(26) Holland, D.; Hannon, A. C.; Smith, M. E.; Johnson, C. E.; Thomas, M. F.; Beesley, A. M. The Role of  $Sb^{5+}$  in the Structure of  $Sb_2O_3-B_2O_3$  Binary Glasses—an NMR and Mössbauer Spectroscopy Study. Solid State Nucl. Magn. Reson. **2004**, 26, 172–179.

(27) Falcão-Filho, E. L.; de Araújo, C. B.; Bosco, C. A. C.; Maciel, G. S.; Acioli, L. H.; Nalin, M.; Messaddeq, Y. Antimony Orthophosphate Glasses with Large Nonlinear Refractive Indices, Low Two-Photon Absorption Coefficients, and Ultrafast Response. J. Appl. Phys. 2004, 97, No. 013505.

(28) Jagannath, G.; Eraiah, B.; NagaKrishnakanth, K.; Venugopal Rao, S. Linear and Nonlinear Optical Properties of Gold Nanoparticles Doped Borate Glasses. *J. Non-Cryst. Solids* **2018**, *482*, 160– 169.

(29) Som, T.; Karmakar, B. Structure and Properties of Low Phonon Antimony Glasses in the  $K_2O-B_2O_3-Sb_2O_3-ZnO$  System. J. Am. Ceram. Soc. **2009**, 92, 2230–2236.

(30) Som, T.; Karmakar, B. Infrared-to-Red Upconversion Luminescence in Samarium-Doped Antimony Glasses. *J. Lumin.* **2008**, *128*, 1989–1996.

(31) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. Van. Sensitive Measurement of Optical Nonlinearities Using a Single Beam. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.

(32) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling One- and Two-Dimensional Solid-State NMR Spectra. *Magn. Reson. Chem.* **2002**, 40, 70–76.

(33) Subhadra, M.; Kistaiah, P. Effect of  $Bi_2O_3$ content on Physical and Optical Properties of  $15Li_2O-15K_2O-xBi_2O_3-(65-x)$   $B_2O_3$ :  $5V_2O_5$  glass System. *Phys. B* **2011**, 406, 1501–1505.

(34) Saritha, D.; Markandeya, Y.; Salagram, M.; Vithal, M.; Singh, A. K.; Bhikshamaiah, G. Effect of Bi<sub>2</sub>O<sub>3</sub> on Physical, Optical and Structural Studies of ZnO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> Glasses. *J. Non-Cryst. Solids* **2008**, *354*, 5573-5579.

(35) Gao, G.; Hu, L.; Fan, H.; Wang, G.; Li, K.; Feng, S.; Fan, S.; Chen, H. Effect of  $Bi_2O_3$  on Physical, Optical and Structural Properties of Boron Silicon Bismuthate Glasses. *Opt. Mater.* **2009**, 32, 159–163.

(36) Rouxel, T. Elastic Properties and Short-to Medium-Range Order in Glasses. J. Am. Ceram. Soc. 2007, 90, 3019–3039.

(37) Gaddam, A.; Fernandes, H. R.; Tulyaganov, D. U.; Pascual, M. J.; Ferreira, J. M. F. Role of Manganese on the Structure, Crystallization and Sintering of Non-Stoichiometric Lithium Disilicate Glasses. *RSC Adv.* **2014**, *4*, 13581–13592.

(38) Widanarto, W.; Sahar, M. R.; Ghoshal, S. K.; Arifin, R.; Rohani, M. S.; Hamzah, K.; Jandra, M. Natural  $Fe_3O_4$  Nanoparticles Embedded Zinc-tellurite Glasses: Polarizability and Optical Properties. *Mater. Chem. Phys.* **2013**, *138*, 174–178.

(39) Davis, E. A.; Mott, N. F. Conduction in Non-Crystalline Systems V. Conductivity, Optical Absorption and Photoconductivity in Amorphous Semiconductors. *Philos. Mag.* **1970**, *22*, 0903–0922.

(40) Bjoern, O. M.; Larry, W. F.; David, V.; Friedrich, A. S. Curvefitting of Raman spectra of silicate glasses. *Am. Mineral.* **1982**, *67*, 686–695.

(41) Meera, B. N.; Ramakrishna, J. Raman Spectral Studies of Borate Glasses. J. Non-Cryst. Solids **1993**, 159, 1.

(42) Dwivedi, B. P.; Khanna, B. N. Cation Dependence of Raman Scattering in Alkali Borate Glasses. *J. Phys. Chem. Solids* **1995**, *56*, 39–49.

(43) Svenson, M. N.; Youngman, R. E.; Yue, Y.; Rzoska, S. J.; Bockowski, M.; Jensen, L. R.; Smedskjaer, M. M. Volume and Structural Relaxation in Compressed Sodium Borate Glass. *Phys. Chem. Chem. Phys.* **2016**, *18*, 29879–29891.

(44) Yadav, A. K.; Singh, P. A Review of the Structures of Oxide Glasses by Raman Spectroscopy. *RSC Adv.* **2015**, *5*, 67583–67609.

(45) Padmaja, G.; Kistaiah, P. Infrared and Raman Spectroscopic Studies on Alkali Borate Glasses: Evidence of Mixed Alkali Effect. J. Phys. Chem. A 2009, 113, 2397–2404.

(46) Kamitsos, E. I.; Karakassides, M. A.; Chryssikos, G. D. Vibrational Spectra of Magnesium-Sodium-Borate Glasses. *J. Phys. Chem.* **1987**, *91*, 1073–1079.

(47) Franco, D. F.; Sant'Ana, A. C.; De Oliveira, L. F. C.; Silva, M. A. P. The  $Sb_2O_3$  Redox Route to Obtain Copper Nanoparticles in Glasses with Plasmonic Properties. *J. Mater. Chem. C* **2015**, *3*, 3803–3808.

(48) Dubois, B.; Videau, J. J.; Couzi, M.; Portier, J. Structural Approach of the  $(xPbCl_2-(1-x)Sb_2O_3)$  Glass System. J. Non-Cryst. Solids 1986, 88, 355–365.

(49) Flower, G. L.; Baskaran, G. S.; Reddy, M. S.; Veeraiah, N. The Structural Investigations of  $PbO-P_2O_5-Sb_2O_3$  Glasses with  $MoO_3$  as Additive by Means of Dielectric, Spectroscopic and Magnetic Studies. *Phys. B* **2007**, 393, 61–72.

(50) Reddy, M. S.; Krishna, G. M.; Veeraiah, N. Spectroscopic and Magnetic Studies of Manganese Ions in ZnO–Sb<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> glass System. *J. Phys. Chem. Solids* **2006**, *67*, 789–795.

(51) Sen, S.; Xu, Z.; Stebbins, J. Temperature Dependent Structural Changes in Borate, Borosilicate and Boroaluminate Liquids: High-Resolution <sup>11</sup>B, <sup>29</sup>Si and <sup>27</sup>Al NMR Studies. *J. Non-Cryst. Solids* **1998**, 226, 29–40.

(52) Frederiksen, K. F.; Januchta, K.; Mascaraque, N.; Youngman, R. E.; Bauchy, M.; Rzoska, S. J.; Bockowski, M.; Smedskjaer, M. M. Structural Compromise between High Hardness and Crack Resistance in Aluminoborate Glasses. *J. Phys. Chem. B* **2018**, *122*, 6287–6295.

(53) Kapoor, S.; Januchta, K.; Youngman, R. E.; Guo, X.; Mauro, J. C.; Bauchy, M.; Rzoska, S. J.; Bockowski, M.; Jensen, L. R.; Smedskjaer, M. M. Combining High Hardness and Crack Resistance in Mixed Network Glasses through High-Temperature Densification. *Phys. Rev. Mater.* **2018**, *2*, No. 063603.

(54) Stebbins, J. F.; Zhao, P.; Kroeker, S. Non-Bridging Oxygens in Borate Glasses: Characterization by <sup>11</sup>B and <sup>17</sup>O MAS and 3Q MAS NMR. *Solid State Nucl. Magn. Reson.* **2000**, *16*, 9–19.

(55) Youngman, R. E.; Zwanziger, J. W. Network Modification in Potassium Borate Glasses: Structural Studies with NMR and Raman Spectroscopies. *J. Phys. Chem.* **1996**, *100*, 16720–16728.

(56) Pascuta, P.; Culea, E. Structural and Thermal Properties of Some Zinc Borate Glasses Containing Gadolinium Ions. *J. Mater. Sci.: Mater. Electron.* **2011**, *22*, 1060–1066.

(57) Youngman, R. E.; Sen, S.; Cornelius, L. K.; Ellison, A. J. G. Novel Structural Aspects of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> Glasses. *Phys. Chem. Glasses* **2003**, *44*, 69–74.

(58) Angeli, F.; Delaye, J. M.; Charpentier, T.; Petit, J. C.; Ghaleb, D.; Faucon, P. Influence of Glass Chemical Composition on the Na-O Bond Distance: A <sup>23</sup>Na 3Q-MAS NMR and Molecular Dynamics Study. *J. Non-Cryst. Solids* **2000**, *276*, 132–144.

(59) Kumar, R. S. S.; Rao, S. V.; Giribabu, L.; Rao, D. N. Femtosecond and Nanosecond Nonlinear Optical Properties of Alkyl Phthalocyanines Studied Using Z-Scan Technique. *Chem. Phys. Lett.* **2007**, 447, 274–278.

(60) Kolavekar, S. B.; Ayachit, N. H.; Jagannath, G.; NagaKrishnakanth, K.; Rao, S. V. Optical, Structural and Near-IR NLO Properties of Gold Nanoparticles Doped Sodium Zinc Borate Glasses. *Opt. Mater.* **2018**, *83*, 34–42.

(61) Manzani, D.; de Araújo, C. B.; Boudebs, G.; Messaddeq, Y.; Ribeiro, S. J. L. The Role of  $Bi_2O_3$  on the Thermal, Structural, and Optical Properties of Tungsten-Phosphate Glasses. *J. Phys. Chem. B* **2013**, *117*, 408–414.

(62) White, W. T.; Smith, W. L.; Milam, D. Direct Measurement of the Nonlinear Refractive-Index Coefficient  $\gamma$  at 355 nm in Fused Silica and in BK–10 Glass. *Opt. Lett.* **1984**, *9*, 10–12.

(63) Gomes, A. S. L.; Falcão Filho, E. L.; de Araújo, C. B.; Rativa, D.; de Araujo, R. E.; Sakaguchi, K.; Mezzapesa, F. P.; Carvalho, I. C. S.; Kazansky, P. G. Third-Order Nonlinear Optical Properties of Bismuth-Borate Glasses Measured by Conventional and Thermally Managed Eclipse Z Scan. J. Appl. Phys. 2007, 101, No. 033115.

(64) Zhang, Y.; Zhang, J.; Jin, Y.; Zhang, J.; Hu, G.; Lin, S.; Yuan, R.; Liang, X.; Xiang, W. Construction and Nonlinear Optical Characterization of CuO Quantum Dots Doped  $Na_2O-CaO-B_2O_3-SiO_2$  bulk Glass. J. Mater. Sci.: Mater. Electron. **2017**, 28, 13201–13208.

(65) Lin, T.; Yang, Q.; Si, J.; Chen, T.; Chen, F.; Wang, X.; Hou, X.; Hirao, K. Ultrafast Nonlinear Optical Properties of Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> oxide Glass. *Opt. Commun.* **2007**, *275*, 230–233.

(66) Sugimoto, N.; Kanbara, H.; Fujiwara, S.; Tanaka, K.; Hirao, K. Ultrafast Response of Third-Order Optical Nonlinearity in Glasses Containing Bi<sub>2</sub>O<sub>3</sub>. *Opt. Lett.* **1996**, *21*, 1637–1639.

(67) Yu, B. L.; Bykov, A. B.; Qiu, T.; Ho, P. P.; Alfano, R. R.; Borrelli, N. Femtosecond Optical Kerr Shutter Using Lead-bismuthgallium Oxide Glass. *Opt. Commun.* **2003**, *215*, 407-411.

(68) Stebbins, J. F.; Zhao, P.; Kroeker, S. Non-Bridging Oxygens in Borate Glasses: Characterization by<sup>11</sup>B and <sup>17</sup>O MAS and 3QMAS NMR. Solid State Nucl. Magn. Reson. **2000**, 16, 9–19.

(69) Masuda, H.; Ohta, Y.; Morinaga, K. Structure of Binary Antimony Oxide Glass. J. Jpn. Inst. Met. 1995, 59, 31-36.

(70) Som, T.; Karmakar, B. Structure and Properties of Low-Phonon Antimony Glasses and Nano Glass-Ceramics in  $K_2O-B_2O_3-Sb_2O_3$  System. J. Non-Cryst. Solids **2010**, 356, 987–999.

(71) Jansen, V. M. The Crystal Structure of Antimony (V) Oxide. Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater. 1979, 35, 539–542.

(72) Doweidar, H. Structural Study of Density and Refractive Index of Sb<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> Glasses. J. Non-Cryst. Solids **2015**, 429, 112-117.

(73) Ok, K. M.; Gittens, A.; Zhang, L.; Halasyamani, P. S. Synthesis, Structure and Characterization of Two New Antimony Oxides – LaSb<sub>3</sub>O<sub>9</sub> and LaSb<sub>5</sub>O<sub>12</sub>: Formation of LaSb<sub>5</sub>O<sub>12</sub> from the Reaction of LaSb<sub>3</sub>O<sub>9</sub> with Sb<sub>2</sub>O<sub>3</sub>. *J. Mater. Chem.* **2004**, *14*, 116–120.

(74) Reddy, M. S.; Raju, G. N.; Nagarjuna, G.; Veeraiah, N. Structural Influence of Aluminium, Gallium and Indium Metal Oxides by Means of Dielectric and Spectroscopic Properties of  $CaO-Sb_2O_3-B_2O_3$  Glass System. J. Alloys Compd. **2007**, 438, 41–51.

(75) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr., Sect. A: Found. Adv.* **1976**, *32*, 751–767.

(76) Nasu, H.; Sugimoto, O.; Matsuoka, J.; Kamiya, K. Non-Resonant-Type Third-Order Optical Non-Linearity of Alkali Silicate and Alkali Aluminosilicate Glasses — Contribution of Individual Chemical Species in the Glasses to  $\chi^{(3)}$ . J. Non-Cryst. Solids 1995, 182, 321–327.

(77) Zhu, X.; Li, Q.; Ming, N.; Meng, Z. Origin of Optical Nonlinearity for PbO, TiO<sub>2</sub>, K<sub>2</sub>O, and SiO<sub>2</sub> Optical Glasses. *Appl. Phys. Lett.* **1997**, *71*, 867–869.

(78) Karthikeyan, B.; Sandeep, C. S. S.; Cha, J.; Takebe, H.; Philip, R.; Mohan, S. Optical Properties and Ultrafast Optical Nonlinearity of Bismuthate Glasses Doped Sodium Borate and Optical Properties and Ultrafast Optical Nonlinearity of Yb<sup>3+</sup> Doped Sodium Borate and Bismuthate Glasses. J. Appl. Phys. **2008**, 103, No. 103509.

(79) Kim, S.-H.; Yoko, T. Nonlinear Optical Properties of TeO<sub>2</sub>-Based Glasses: MOx-TeO<sub>2</sub> (M = Sc, Ti, V, Nb, Mo, Ta, and W) Binary Glasses. J. Am. Ceram. Soc. **1995**, 78, 1061–1065.

(80) Hashimoto, T.; Yoko, T. Third-Order Nonlinear Optical Properties of Sol–gel-Derived  $V_2O_5$ , Nb<sub>2</sub>O<sub>5</sub>, and Ta<sub>2</sub>O<sub>5</sub> Thin Films. *Appl. Opt.* **1995**, *34*, 2941–2948.

(81) Mozzi, R. L.; Warren, B. E. The Structure of Vitreous Boron Oxide. J. Appl. Crystallogr. 1970, 3, 251–257.