Role of Neodymium on Some Acoustic and Physical Properties of Bi\textsubscript{2}O\textsubscript{3} - B\textsubscript{2}O\textsubscript{3} - SrO Glasses

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\begin{abstract}
SrO-Bi\textsubscript{2}O\textsubscript{3} - B\textsubscript{2}O\textsubscript{3} glass systems with different content of neodymium oxide Nd\textsubscript{2}O\textsubscript{3} were prepared by rapid-quenching technique. On Record FTIR deconvoluted spectra were in the range of 400–2000 cm\textsuperscript{-1}. Some parameters such as; density and molar volume were acquired. Ultrasonic wave velocities (longitudinal and shear) and elastic moduli were acquired. The results were interpreted as due to the role of Nd\textsubscript{2}O\textsubscript{3}. Formation of BO\textsubscript{4} causes an increase in the rigidity of glass, and consequently resulted an increase in the glass density. Increment of molar volume revealed that addition of Nd\textsubscript{2}O\textsubscript{3} results in an extension of glass network. The presence of [BiO\textsubscript{4}] octahedral units builds up the bismuthate structure of investigated glasses. The Nd\textsuperscript{3+} ions caused the proportion of average bonds elongations to diminish from 48.18 % to reach the value of 45.59 % at 5.7 mol. % of Nd\textsubscript{2}O\textsubscript{3}. © 2020 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
\end{abstract}

1. Introduction

Investigation of glass with high ionic conduction gained more industrial attraction in the last decades due to its potential applications, such as nonlinear optics, high energy physics and electrochemical devises for solid electrolytes. Physical properties of glass samples can be improved by the addition of modifiers; such as alkali oxides (Li\textsubscript{2}O, Na\textsubscript{2}O, etc.)\textsuperscript{[1]}, alkaline-earth oxides (SrO, BaO, etc.)\textsuperscript{[2]}, transition metal oxide (ZnO, Cr\textsubscript{2}O\textsubscript{3}, etc.)\textsuperscript{[3]}, other metal oxides (PbO, Bi\textsubscript{2}O\textsubscript{3}, etc.)\textsuperscript{[3,4]}, other non-metal oxides (SiO\textsubscript{2}, B\textsubscript{2}O\textsubscript{3}, TeO\textsubscript{2}, etc.) and rare-earth oxides (Gd\textsubscript{2}O\textsubscript{3}, Sm\textsubscript{2}O\textsubscript{3}, etc.)\textsuperscript{[5]}. 

Borate glass modified with bismuth oxide is characterized by its high dielectric behavior, high density and high refractive index. Strontium doping leads to stable ionic glasses. The borate glass system modified with Bi & Sr has been widely investigated\textsuperscript{[6–8]}. Naidu et al.\textsuperscript{[7]} found that the Bi\textsubscript{2}O\textsubscript{3} acts as a modifier up to 15 mol% and then it might acts as a network former. They showed a better Bi:Al:Sr:B ratio of 20:7:23:50 mol%.

Rare-earth oxide modifiers showed a significant improvement over glass systems. They improve the glass thermal, electrical and optical stability\textsuperscript{[5,7,9]}. Such modifiers received much interest because of their potential use in laser host, tunable fiber grating and wave guides\textsuperscript{[6]}. Studying the mechanical
The performance of glass system is very important to understand the glass formation mechanisms. Ultrasonic method plays a significant role in characterizing the glass network.

The present investigation sheds more light on the structure of Nd modified Bi-Sr-borate glass. It is interesting to study the effect of Nd₂O₃ addition on Bi-Sr-borate glasses for their possible applications in many aspects. The authors reported many structural, experimental and theoretical mechanical properties, and correlated them with the structure of Bi-Sr-borate glasses containing Nd₂O₃. Evaluation of these properties was achieved by measuring and calculating many physical parameters. Theoretical elastic properties were studied by employing both bond compression [10] and Makishima-Mackenzie [11] models. It can give us a guidance to predict glass selection for different applications.

### 2. Experimental techniques

#### 2.1. Glasses preparation

Bi₂O₃-Bi₂O₅-SrO glasses modified with different content of Nd₂O₃ were synthesized by the rapid-quenching technique. Batches of glass samples are tabulated in Table 1. The oxides Bi₂O₃, Bi₂O₅, SrO and Nd₂O₃ of purity 99.9% were used for synthesis this glass system.

Required quantities of powder oxides were weighed using a four-digit balance (HR-200; accuracy ±0.0001 g). Each sample was ground in zirconia mortar grinder (FRITSCHE Pulverisette) for two hours to achieve high homogeneity of the oxide mixture. The mixtures were heated in alumina crucible at 450°C for 1 hr to remove any residual water on powders.

Then the mixtures were melted in a muffle furnace at 1500°C for 1 hr, followed by stirring right away in order to obtain clear homogeneous bubble-free glass in molten liquid form. The molten samples were poured in a preheated steel square mold at 400°C. The samples then were annealed at 550°C for 1 hr and left to cool down to room temperature inside the furnace. The glasses were then polished and polished down to about 1 × 1 × 0.2 cm² with a mirror-finished surface.

The rough polishing was carried out using SiC on a glass plate, followed by final polishing with fine alumina abrasive with particle size less than 0.1 μm. The deviation on the thickness of the samples was found to be ±40 μm.

#### 2.2. Density measurements

The densities (ρ) of the glass samples were measured employing Archimedes technique and toluene as an immersing fluid. The measurements were repeated four times to ensure the results and the variations in densities were about ±10 kg/m³.

### 2.3. Ultrasonic velocity measurements

The ultrasonic velocities were measured using the pulse-echo technique; the ultrasonic waves transmitted from the transducer inside the sample and reflected back from the sample back side. The reflected wave as an echo, appears on a flaw detector screen (GE, USN35) as a sharp peak. The velocities can be calculated by dividing the sample thickness by the wave traveling time inside the sample. Both longitudinal and shear wave times, at room temperature, were measured using 4 MHz Karl Deutsch transducer S12 HB4 and 2 MHz Krautkramer transducer K2KY. The uncertainty of the calculated velocities was less than 5 m/s.

Based on the values of ultrasonic wave velocities and density, the elastic moduli, longitudinal (L), shear (G), bulk (K) and Young's (E) in addition to Poisson ratio (ν) were determined using the relations [12]:

\[
L = \frac{\rho V_l^2}{1} 
\]

\[
G = \frac{\rho V_s^2}{2} 
\]

\[
K = L - \left( \frac{4G}{3} \right) 
\]

\[
E = (1 + \nu)2G 
\]

\[
\nu = \left( \frac{L - 2G}{2(L - G)} \right) 
\]

### 2.4. Fourier Transform Infra-Red studies

Fourier Transform Infra-Red (FTIR) spectra were measured for the glass samples at room temperature in the wavelength range between 400 – 1400 cm⁻¹ by employing KBr disc technique using JASCO, FTIR-430 spectrometer (Japan). The FTIR spectra were normalized to 1 after correcting the background by linear baseline subtraction. The modification was employed to the IR spectra to reduce the effect of sample amount in the KBr discs. Deconvolution of the FTIR absorption spectra was carried out employing Gaussian fitting. The deconvolution allowed us to see more details of structure changes by studying the bonds vibration mechanisms of the borate glass system.

### 3. Results and discussion

#### 3.1. Density and molar volume

The density (ρ) and molar volume (Vₘ) of glass samples are important parameters to characterize the glass structure. The density of the glass system SrO-Bi₂O₃-B₂O₅-Nd₂O₃ exhibits increasing trend from 4356 to 4478 kg/m³ with increasing content of Nd₂O₃, as shown in Table 2 and Fig. 1. Such density increments can be due to the higher molecular weight of Nd₂O₃ (Nd₂O₃ = 336.48 gm/mol, B₂O₃ = 69.62 gm/mol and SrO = 103.6 gm/mol). In addition, increasing the Nd₂O₃...
Table 2 – The values of density (ρ), molecular volume (V_M), molecular weight M_wt, B_2O_3 molar fraction (x_B), the boron atoms molar volume (V_M^{B}) average boron-boron separation \(d_{B-B}\), \(N_{d}^{3+}\) ion concentration (N), internuclear distance (r_i), polaron radius (r_p), field strength (F_s) and the fraction of tetrahedrally coordinated boron atom (N4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ρ (kg/m^3)</th>
<th>V_M (cm^3)</th>
<th>Z</th>
<th>M_wt</th>
<th>x_B (mol%)</th>
<th>V_M^{B} (Å)</th>
<th>(d_{B-B}) (Å)</th>
<th>N x 10^20 (ions/cm^3)</th>
<th>r_i x 10^-7 (cm)</th>
<th>r_p x 10^-8 (cm)</th>
<th>F_s x 10^14 (cm^-2)</th>
<th>N4</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4356</td>
<td>44.84</td>
<td>4.40</td>
<td>195.3</td>
<td>50.0</td>
<td>44.84</td>
<td>4.207</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.528</td>
</tr>
<tr>
<td>b</td>
<td>4377</td>
<td>44.94</td>
<td>4.41</td>
<td>196.7</td>
<td>49.5</td>
<td>44.50</td>
<td>4.196</td>
<td>1.33</td>
<td>1.96</td>
<td>7.9</td>
<td>7.06</td>
<td>0.681</td>
</tr>
<tr>
<td>c</td>
<td>4398</td>
<td>45.03</td>
<td>4.41</td>
<td>198.1</td>
<td>49.0</td>
<td>44.17</td>
<td>4.186</td>
<td>2.62</td>
<td>1.56</td>
<td>6.3</td>
<td>11.13</td>
<td>0.659</td>
</tr>
<tr>
<td>d</td>
<td>4419</td>
<td>45.13</td>
<td>4.42</td>
<td>199.4</td>
<td>48.5</td>
<td>43.85</td>
<td>4.176</td>
<td>3.89</td>
<td>1.37</td>
<td>5.5</td>
<td>14.49</td>
<td>0.659</td>
</tr>
<tr>
<td>e</td>
<td>4449</td>
<td>45.27</td>
<td>4.43</td>
<td>201.4</td>
<td>47.8</td>
<td>43.40</td>
<td>4.161</td>
<td>5.73</td>
<td>1.20</td>
<td>4.9</td>
<td>18.80</td>
<td>0.659</td>
</tr>
<tr>
<td>f</td>
<td>4478</td>
<td>45.40</td>
<td>4.43</td>
<td>203.3</td>
<td>47.2</td>
<td>42.97</td>
<td>4.148</td>
<td>7.51</td>
<td>1.10</td>
<td>4.4</td>
<td>22.56</td>
<td>0.658</td>
</tr>
</tbody>
</table>

Fig. 1 – The variation of glass density and molar volume values with Nd_2O_3 content.

content at the expense of SrO-B_2O_3-B_2O_3 content, which is kept constant, causes a decrease in B atoms but remains O atom constant in the glass network. The result is a change in boron to oxygen ratio that creates BO_4- structural units around Nd_2O_3 [13,14], as will be discussed in the identity of IR bands between 897-886 cm^-1. As a conclusion, forming up BO_4 around Nd_2O_3 increases the glass rigidity and correspondingly increases the density of the glass system SrO-B_2O_3-B_2O_3-Nd_2O_3.

On the other hand, the molar volume (V_M) is observed to increase with adding Nd_2O_3. The ionic radius of Nd (1.29 Å) is larger than those of the other elements (Sr = 1.18 Å, Bi=0.96 Å and B=0.11 Å), therefore the addition of Nd_2O_3 stretches the glass network increasing the molar volume. In addition, the oxygen dissemination in the glass structure is well known to be probed by the molar volume. In other words, V_M is sensitive for the number of nonbridging oxygens (NBOs) in the glass system. As a consequence, growing the NBOs with increasing Nd_2O_3 content in the glass system (as will be discussed in IR section) increases the molar volume. As a final conclusion, addition of Nd_2O_3 results in enlarging glass network [15].

For further understanding of structural changes caused by Nd_2O_3 in the glass system, some related physical properties such as the average value of boron-boron (B-B) separation \(d_{B-B}\), \(N_{d}^{3+}\) ion concentration (N), polaron radius (r_p), internuclear distance (r_i) and field strength (F_s) were calculated by the below equations [16-18] and listed in Table 2.

\[
\langle d_{B-B}\rangle (\text{Å}) = (V_M^{B}/N_A)^{1/3}
\]

(6)

\[
N (\text{ions/cm}^3) = (\text{mol}\% \text{ of Nd} \times N_A \times \rho) / (\text{glass average molecular weight})
\]

(7)

\[
r_p (\text{Å}) = 1/2(\pi/6N)^{1/3}
\]

(8)

\[
r_i (\text{Å}) = (1/N)^{1/3}
\]

(9)

\[
F_s (\text{cm}^{-2}) = Z/r_p^2
\]

(10)

As a definition, \(V_M^{B} = V_M/(1-x_B)\), is the volume that contains one mole of boron atoms within the borate glass structure, x_B is the B_2O_3 molar fraction and N_A is the Avogadro’s number.

As in Table 2, \(d_{B-B}\) shows a decrease trend which denotes the increase in compactness of glass network by decreasing the boron atoms molar volume. This result supports the increase in density of the glass samples. From Table 2, it’s also observed that r_p and r_i decrease with Nd_2O_3 content which are related to increase of \(N_{d}^{3+}\) ion concentration (N). Decreases in
both \( r_p \) and \( r_l \), which mean a decrease in distance between Nd and O atoms, increase the Nd–O bond strength. The strengthening of Nd–O bonds directly increases \( f_5 \) which also supports the increments in the glass density.

### 3.2. FT-IR studies

Fig. 2 shows FTIR measurements for all glass samples in range 400-1700 cm\(^{-1} \) at room temperature. Deconvolutions of the FTIR spectra were done for all samples. Fig. 3 shows the deconvoluted FTIR spectrum of 0 and 1 mol% \( \text{Nd}_2\text{O}_3 \) samples as patterns. The parameters of deconvoluted bands of all samples are tabulated in Table 3, and their assignments are summarized in Table 4.

The band at 466 cm\(^{-1} \), assigned to the Bi–O–Bi stretching vibration of distorted octahedral [\( \text{BiO}_6 \)] units [19], [20] increases in intensity and shifts to high and then low wave numbers with \( \text{Nd}_2\text{O}_3 \) content. Since the [\( \text{BiO}_2 \)] polyhedra vibration band at 840 cm\(^{-1} \) [21] does not appear in the IR absorption, it can be concluded that only [\( \text{BiO}_6 \)] octahedral units build up the bismuthate structure of investigated glasses.

Because of the asymmetry of the crystal field at Nd site, some of Nd\(^{3+} \) ions might be covered by bismuth groups [22], giving rise to intensification of the distorted [\( \text{BiO}_6 \)] IR band. The non-symmetric component of electric field acting on Nd\(^{3+} \) ion enhances with increasing content of \( \text{Nd}_2\text{O}_3 \) [23]. This may be due to the formation of NBOs around Nd\(^{3+} \) ions. The creation of NBOs from bridging oxygens increases the bond asymmetry of the neighboring cations.

Shifting the band at first to high wave number may be due to the high ionicity of the Nd\(^{3+} \) ion with \( \sim 1 \text{ mol}\% \text{Nd}_2\text{O}_3 \) [23]. Increasing the \( \text{Nd}_2\text{O}_3 \) content \( \geq 2 \text{ mol}\% \) enhances the covalency of the Nd–O bond intensifying the bismuth bonding defects and NBOs [24]. As a consequence, the electrons rearrangement degree raises and herewith increases the donor centers in the glass matrix [25]. The average bond energy of the bismuth groups accordingly decreases, shifting the IR band to low wave number.

The band appears at 712 cm\(^{-1} \) assigned to the bending vibration of B–O–B in [\( \text{BO}_3 \)] units [21,26–29]. The observed shift

![Fig. 3 - The deconvolution data of the FTIR absorption spectra a) 0 mol.%, b) 1 mol. % \( \text{Nd}_2\text{O}_3 \).](image)

| Table 3 – FT-IR deconvoluted bands center and area. |
|---|---|---|---|---|---|---|
|   | Band 1 | Band 2 | Band 3 | Band 4 | Band 5 | Band 6 |
| A% | C   | A% | C   | A% | C   | A% |
| Area% | 46.6 | 15.8 | 702 | 1.1 | 897 | 3.69 |
| C   | 482 | 24.86 | 715 | 5.7 | 928 | 35.51 |
| Band 1 | 475 | 24.54 | 2.39 | 887 | 10.07 | 10.41 |
| Band 2 | 473 | 24.5 | 2.19 | 2.18 | 10.39 | 10.39 |
| Band 3 | 472 | 24.41 | 2.08 | 886 | 10.39 | 10.39 |
| Band 4 | 471 | 24.34 | 1.98 | 886 | 10.39 | 10.39 |
| Band 5 | C   | A% | C   | A% | C   | A% |
| Band 6 | 1223 | 21.76 | 1234 | 6.66 | 1234 | 6.66 |
| Band 7 | 1309 | 1.48 | 1359 | 11.02 | 1243 | 11.02 |
| Band 8 | 1462 | 1.48 | 1352 | 10.43 | 1243 | 10.43 |
| Band 9 | 1609 | 0.36 | 1604 | 0.91 | 1602 | 0.52 |
| A% | 10.42 | 3.38 | 3.97 | 5.61 | 7.01 | 7.01 |
| C   | 1610 | 35.51 | 1602 | 0.91 | 1602 | 0.52 |
| Band 7 | 1609 | 0.36 | 1604 | 0.91 | 1602 | 0.52 |

A% = Area%., C = Band center wavenumber.
Table 4 – Assignment of FT-IR bands.

<table>
<thead>
<tr>
<th>No.</th>
<th>the band at (cm⁻¹)</th>
<th>Deconvolution components (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>400-800</td>
<td>466 483 475 473 472</td>
<td>~460 Bi-O bond in BiO₆ octahedral unit overlapped with Si-O-Si and O-Si-O bending modes of bridging oxygens (Q₆) [39]. Bending modes of B-O-B.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>702 715 720 721 721</td>
<td>Si-O-B symmetric stretching of bridging oxygens.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>774 795 795 795 795</td>
<td>~900-885 stretching vibrations of tetrahedral BO₄ units.</td>
</tr>
<tr>
<td></td>
<td>800-1200</td>
<td>897 890 887 887 886</td>
<td>~1000 di-borate groups ~1080 penta-borate groups overlapped with asymmetric stretching vibrations of NBO of SiO₄ tetrahedra (Q₄) [39].</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1040 1043 1041 1041 1040</td>
<td>~1207-1246 stretching vibrations of the B-O bonds of (BO₃)³⁻ unit from the boroxol rings.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1223 1237 1234 1234 1234</td>
<td>~1248-1343 stretching vibrations of the B-O bonds of (BO₃)³⁻ unit from various types of borate groups [33].</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1309 1367 1359 1352 1350</td>
<td>~1479-1429 anti-symmetrical stretching vibrations with three NBOs of the B-O-B groups.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1451 1483 1485 1482 1482</td>
<td></td>
</tr>
</tbody>
</table>

of this band from 702 to 721 cm⁻¹ may be attributed to the entering of Nd³⁺ ions of high ionic radius in the B-O long chains, in lieu of the interstitial sites, which decreases their bond lengths, as stated above in the effect of Nd on d₉₈₂₆. As a result, the bending energy of BO₃ vibration increases at some extent at the Nd³⁺ sites shifting the band to higher wave numbers.

Bands between 897-886 cm⁻¹ are due to the stretching vibration of [BO₄] units [10,27,28,30,31]. Larger increases in their intensities are observed with increasing content of Nd₂O₃. It has been reported that a rare earth ion is coordinated by four BO₄ tetrahedra so that the two sets of two opposite tetrahedral are in similar position relative to the rare earth ion and retain the eight-coordination of the metal ion by NBOs (two oxygen ions contributed by each tetrahedron) [32].

Bands between 1220 and 1350 cm⁻¹ are contributed to the stretching vibration of [BO₃] units [33–36]. A larger shift is observed from 1309 to 1350 cm⁻¹ with increasing content of Nd₂O₃. Nd-O bonds are of higher energy than those of Bi-O and Sr-O. In addition, decrease in Nd-O bond length (decrease in r₁ and r₂) increases its bond strength significantly which enhances the stretching frequency of Nd-O-B. The result is the shifts of the IR bands of [BO₃] units to higher wave numbers.

By summing the areas of the bands among 800 -1200 cm⁻¹ [BO₄ units] and the bands among 1200 – 1600 cm⁻¹ [BO₃ units], the fraction of the 4-coordinated boron atoms N₄ was computed and noticed to increase as recorded in Table 2. The N₄ results along with the presence of Bi atoms as BiO₆ units matched with results discussed in section 3.1, giving the conclusion of increased rigidity of these structures by increasing content of Nd₂O₃.

3.3. Ultrasound mechanical characterizations

The ultrasonic pulse-echo technique is convenient technique to estimate the elastic behavior of glassy systems. Using data of the ultrasonic velocities and densities, moduli of longitudinal, shear, young’s and bulk in addition to Poisson’s ratio can be calculated [37].

Both longitudinal Vₐ and shear Vₛ velocities show a linear decrease behavior with Nd₂O₃ content, Fig. 4. Vₐ and Vₛ decrease from 4544 to 4498 m/s and from 3017 to 2983 m/s with increasing content of Nd₂O₃ from 0 mol% to 5.7 mol%, respectively. The decrease may be due to the rise of NBOs as stated above.

Debye temperature θ₀ is the temperature at which almost all vibrational modes are excited. Softening temperature Tₛ is defined as the temperature in which viscous flow turns to plastic flow. The values of Tₛ, θ₀ and the mean ultrasonic velocity Vₘₐₜ can be calculated using the equations (11,12 and 13) [38,39]. The values are shown in Fig. 5 and tabulated in the Table 5.

\[
T_s = \frac{V_m M}{C^2Z_g}, \quad (11)
\]

\[
\theta_0 = \left( \frac{\hbar}{K_B} \right) \left( \frac{3Z_g N_A}{4\pi V_m} \right)^{1/3}, \quad (12)
\]

\[
V_{mean} = \left( \frac{1}{3} \left( \frac{V_L}{V_L} + \frac{V_T}{V_T} \right) \right)^{-1/3}, \quad (13)
\]

where M is the effective molecular weight, Z_g is the atoms number in the glass system, C = 507.4 K1/2 m/s for borate glasses is a constant of proportionality, Vₛ is the mean atomic
Table 5 – Density (ρ), molar volume (V_m), longitudinal velocity (V_L), shear velocity (V_S), mean ultrasonic velocity (V_mean), Debye temperature (θ_D) and Softening temperature (T_s).

<table>
<thead>
<tr>
<th>ρ (kg/m³)</th>
<th>V_m (cm³/mol)</th>
<th>V_L (m/s)</th>
<th>V_S (m/s)</th>
<th>V_mean (m/s)</th>
<th>θ_D (K)</th>
<th>T_s (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4356</td>
<td>44.84</td>
<td>4544</td>
<td>2727</td>
<td>3017</td>
<td>349.87</td>
</tr>
<tr>
<td>b</td>
<td>4377</td>
<td>44.94</td>
<td>4535</td>
<td>2721</td>
<td>3010</td>
<td>349.00</td>
</tr>
<tr>
<td>c</td>
<td>4398</td>
<td>45.04</td>
<td>4526</td>
<td>2716</td>
<td>3005</td>
<td>348.26</td>
</tr>
<tr>
<td>d</td>
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<td>45.13</td>
<td>4517</td>
<td>2710</td>
<td>2998</td>
<td>347.40</td>
</tr>
<tr>
<td>e</td>
<td>4449</td>
<td>45.27</td>
<td>4508</td>
<td>2703</td>
<td>2990</td>
<td>346.39</td>
</tr>
<tr>
<td>f</td>
<td>4478</td>
<td>45.40</td>
<td>4498</td>
<td>2696</td>
<td>2983</td>
<td>345.39</td>
</tr>
</tbody>
</table>

Fig. 5 – Variation of mean ultrasonic velocity V_mean, Debye temperature θ_D, and Softening temperature T_s with Nd$_2$O$_3$ content.

Fig. 6 – Variation of experimental values of Young’s modulus E, shear modulus G, longitudinal modulus L, Bulk modulus K for the glass samples.

volume, h is the Planck’s constant, K_B is the Boltzmann’s constant and N_A is the Avogadro’s number.

It is observed that both V_m and θ_D decrease from 3017 to 2983 m/s and from 349.8 to 345.4 K with increasing content of Nd$_2$O$_3$ from 0 mol% to 5.7 mol%, respectively. This is owing to the rise of NBOs with Nd$_2$O$_3$. This is agreed with the previously reported results by other researchers [38, 40]. On the other hand, T_s increases with increasing of Nd in the borate glass matrix. This increment means more stability of the elastic properties of the glass structure system.

The Young’s modulus is the ratio between the linear stress and linear strain, and it is associated with the bond strength. Also, the bulk modulus is defined as the ratio of volume change to the applied force on it all directions. It is noticed that the elastic moduli values increase linearly with increasing content of Nd$_2$O$_3$ in the glass system. The elastic moduli increase from 78.95 to 79.40, 32.39 to 32.55, 89.94 to 90.60 and 46.75 to 47.20 GPa for E, G, L and K, respectively. All the data are illustrated in Fig. 6 and tabulated in Table 6. The increase in elastic moduli is due to the rise of [BO$_4$] units that are enhancing the number of bonds per unit volume n_b and progressively growing the crosslink density n_c and then the glass density, Table 7. The increments in elastic moduli also may be attributed to the increase of anharmonic electron-phonon interactions resulting from improvement of the borate glass structure modified by Nd ions. This modification amplifies the oxygen vibrations amplitude so that the vibration of anion mass ratio to the mass of various cations is reduced. Also, Nd$_2$O$_3$ slightly improves the hardness (H) of the glass structure, see Table 6. Precisely, addition of 2 mol. % Nd$_2$O$_3$ hardens the glass system B$_2$O$_3$-B$_2$O$_3$-SrO. It is noted that all values of Poisson’s ratio are less than 0.3. That indicates a relatively high cross-linked density. Moreover, the increase in Poisson’s ratio values shows the gaining of the structural bonds and increases the system rigidity with increasing content of Nd$_2$O$_3$ [1].

3.4. Theoretical models

Bond compression and Makishima-Mackenzie models are the most two theoretical models applied to locate the mechanical behavior of the glass system. These models depend on the coordination number of cations, number of networks per unit volume, the type of bonds, backing density and the oxide constituent’s dislocation energy.

The average stretching force constant F is estimated by

$$ F = \sum x_i n_i f_i \left( \sum i n_i \right) $$

where x is the mole fraction of the component oxide i, n_i is the number of network bonds per unit formula, r is the length of cation-anion bond and f is the bond stretching force constant and can be determined using [41],

$$ f = 17/r^3 $$
The bond compression force constant is inversely proportional to the bond length and the difference in electronegativity between the former (B) and modifier (Nd), which reflects reduction in f with increasing Nd content.

The bond compression bulk modulus \( K_{bc} \) [41] and the number of network bonds per unit volume \( (n_b) \) are given by

\[
K_{bc} = N_a 9 V_M \sum \text{i} \left\{ x n_f f^2 \right\}_i
\]

(16)

\[
n_b = \sum n_i \left\{ x n_f \right\}_v M = N_a V_M \sum \text{i} \left\{ x n_f \right\}_i
\]

(17)

where \( N_a \) is Avogadro's number, and \( V_M \) is the glass molar volume. The estimated bulk modulus reveals an increase from 52.38 to 53.08 GPa, and it is due to the decrease in the average crosslink density of the glass system under investigation. On the other hand, the ratio between theoretical and experimental values of bulk modulus \( K_{bc}/K_{exp} \) demonstrates a decreasing trend as shown in Fig. 7, consequently decreases the involvement of bond bending processes to isotropic elastic deformation of the glass structure. The doping with the rare-earth Nd in the borate glass shows an increase in \( n_b \) from 6.398 \( \times 10^{25} \) to 6.565 \( \times 10^{25} \) in the cubic meter. All values are found in Table 7.

The average cross-link density of the glass network \( n_{c} \) can be calculated by employing the following equation

\[
\pi_c = 1/\eta \sum \text{i} (n_c)_i (N_c)_i
\]

(18)

where \( n_c \) is the number of cross-links per cation (cross-link density) in the oxide \( i \), and \( \eta \) is the total number of cations per glass formula unit. The \( n_c \) is profoundly affected by the difference between modifier coordination number concerning the glass network's main former. In other words, it increases when adding a modifier with higher coordination number over a former with lower coordination. It increases as modifier to former ratio increases.

**Table 6** - Experimental values of Young’s modulus (E), shear modulus (G), longitudinal modulus (L), Bulk modulus (K), Poisson’s ratio (\( \nu \)), E/G ratio and microhardness (H).

<table>
<thead>
<tr>
<th></th>
<th>E (GPa)</th>
<th>G (GPa)</th>
<th>L (GPa)</th>
<th>K (GPa)</th>
<th>( \nu )</th>
<th>E/G</th>
<th>H (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>78.95</td>
<td>32.39</td>
<td>89.94</td>
<td>46.75</td>
<td>0.2186</td>
<td>2.4371</td>
<td>6.078</td>
</tr>
<tr>
<td>b</td>
<td>79.00</td>
<td>32.41</td>
<td>90.03</td>
<td>46.81</td>
<td>0.2188</td>
<td>2.4375</td>
<td>6.077</td>
</tr>
<tr>
<td>c</td>
<td>79.08</td>
<td>32.45</td>
<td>90.10</td>
<td>46.84</td>
<td>0.2186</td>
<td>2.4372</td>
<td>6.086</td>
</tr>
<tr>
<td>d</td>
<td>79.11</td>
<td>32.45</td>
<td>90.16</td>
<td>46.89</td>
<td>0.2188</td>
<td>2.4376</td>
<td>6.084</td>
</tr>
<tr>
<td>e</td>
<td>79.27</td>
<td>32.51</td>
<td>90.41</td>
<td>47.07</td>
<td>0.2193</td>
<td>2.4387</td>
<td>6.082</td>
</tr>
<tr>
<td>f</td>
<td>79.40</td>
<td>32.55</td>
<td>90.60</td>
<td>47.20</td>
<td>0.2197</td>
<td>2.4399</td>
<td>6.083</td>
</tr>
</tbody>
</table>

**Table 7** - Theoretical bond compression bulk modulus \( K_{bc} \), ratio \( K_{bc}/K_{exp} \), number of bonds per unit volume \( (n_b) \), average ring diameter \( (f) \), average stretching force constant \( (F) \), average cross-link density \( (n_c) \) and theoretically calculated Poisson’s ratio \( (\nu_{th}) \).

<table>
<thead>
<tr>
<th></th>
<th>( K_{bc} ) (GPa)</th>
<th>( K_{bc}/K_{exp} )</th>
<th>( n_b \times 10^{25} ) (m(^{-3}))</th>
<th>( f ) (nm)</th>
<th>( F ) (N ( \cdot ) m(^{-1}))</th>
<th>( n_c )</th>
<th>( \nu_{th} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>63.25</td>
<td>1.353</td>
<td>6.398</td>
<td>4.866</td>
<td>277</td>
<td>2.63</td>
<td>0.2199</td>
</tr>
<tr>
<td>b</td>
<td>64.06</td>
<td>1.368</td>
<td>6.514</td>
<td>4.818</td>
<td>267</td>
<td>2.74</td>
<td>0.2177</td>
</tr>
<tr>
<td>c</td>
<td>63.94</td>
<td>1.365</td>
<td>6.513</td>
<td>4.822</td>
<td>269</td>
<td>2.75</td>
<td>0.2174</td>
</tr>
<tr>
<td>d</td>
<td>63.81</td>
<td>1.361</td>
<td>6.529</td>
<td>4.806</td>
<td>265</td>
<td>2.78</td>
<td>0.2169</td>
</tr>
<tr>
<td>e</td>
<td>63.56</td>
<td>1.350</td>
<td>6.549</td>
<td>4.773</td>
<td>259</td>
<td>2.81</td>
<td>0.2163</td>
</tr>
<tr>
<td>f</td>
<td>63.41</td>
<td>1.343</td>
<td>6.565</td>
<td>4.753</td>
<td>256</td>
<td>2.84</td>
<td>0.2156</td>
</tr>
</tbody>
</table>

**Fig. 7** - Variation of experimental bulk modulus, theoretical bond compression bulk modulus and ratio of theoretical to experimental as a function of \( \text{Nd}_2\text{O}_3 \) content, the line has been drawn to guide the eyes.

The average atomic ring size \( (\ell) \) according to the ring deformation model can be expressed in the form [42]

\[
K_e = \frac{0.0106 F_b}{\ell^{3.84}}
\]

(19)

where \( F_b \) is the bond bending force constant, and \( K_e \) is the experimental bulk modulus. Nevertheless, the average ring size \( \ell \) shows a continues decrease from 4.866 to 4.753 with increasing content of \( \text{Nd}_2\text{O}_3 \), it takes the same behavior of the elastic modulus. More oxygen compactness around \( \text{Nd}_2\text{O}_3 \) forms long-chain rings more than going interstitially inside the borate rings. The data are in good agreement with previously published articles [6].
The calculated mechanical constants $G_{th}$, $L_{th}$ and $E_{th}$ moduli tend to rise from 36.1 to 37.3, 100.4 to 102.6, and 88.0 to 90.6 respectively, which are in agreement with the experimental results. The mechanical behavior is greatly dependent of $n_c$ and $\theta_0$. That is to say the calculated $G_{th}$, $L_{th}$ and $E_{th}$ show increasing trends matching with $n_c$ and $\theta_0$, which are in a good agreement with the experimental data. These values depend on the dissociation energy and packing density. The theoretical mechanical behavior data are in Table 8. The difference between the theoretical and experimental values of bulk modulus is owing to the high number of network bonds in the glass system. However, the Poisson’s ratio shows a decreasing trend, which is owing to the loosely packed oxide glass atoms due to the Nd doping.

3.5. Theoretically treated analysis of longitudinal vibrations

A model of Central force [3], [45] is hired to portray the anion atom longitudinal vibrations among two cations (A – O – A), or a cation atom among two anions (O – A – O) detached by a space $R_O$ in the glass network Bi$_2$O$_3$ - B$_2$O$_3$ - SrO glasses

<table>
<thead>
<tr>
<th>$E_{th}$ (GPa)</th>
<th>$L_{th}$ (GPa)</th>
<th>$G_{th}$ (GPa)</th>
<th>$K_{th}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 88.01</td>
<td>100.35</td>
<td>36.07</td>
<td>52.38</td>
</tr>
<tr>
<td>b 88.98</td>
<td>101.12</td>
<td>36.53</td>
<td>52.53</td>
</tr>
<tr>
<td>c 89.10</td>
<td>101.23</td>
<td>36.59</td>
<td>52.55</td>
</tr>
<tr>
<td>d 89.42</td>
<td>101.50</td>
<td>36.74</td>
<td>52.64</td>
</tr>
<tr>
<td>e 90.05</td>
<td>102.13</td>
<td>37.02</td>
<td>52.90</td>
</tr>
<tr>
<td>f 90.57</td>
<td>102.63</td>
<td>37.25</td>
<td>53.08</td>
</tr>
</tbody>
</table>
modified with different content of Nd₂O₃. Fig. 8 shows the mutual potential energies of these longitudinal configurations of the glass compositions 0.3 Bi₂O₃ – 0.5 B₂O₃ – 0.2 SrO – 0.0
Nd₂O₃, 0.294 Bi₂O₃ – 0.49 B₂O₃ – 0.196 SrO – 0.02 Nd₂O₃, 0.287
Bi₂O₃ – 0.479 B₂O₃ – 0.191 SrO – 0.043 Nd₂O₃ and 0.283 Bi₂O₃
– 0.472 B₂O₃ – 0.188 SrO – 0.057 Nd₂O₃, (as exemplifications),
with diverse oxygen atom locations and diverse elongation
proportions. Bonds sorts existent in the glass frameworks are
(B–O–B), (B–O–Sr), (Bi–O–Bi), (Bi–O–Sr), (B–O–Nd), and
(Bi–O–Nd).

For the Nd₂O₃ concentricity range between 0 to 5.7 mol. %,
and at 50 % elongation treatment as an example, the Nd³⁺ ions
causse the proportion of bonds elongations (ε) to decrease
from 48.18 % to reach the value of 45.59 % at 5.7 mol. % of Nd₂O₃
content as represented in Fig. 9. Such results may explain the
raise of elastic moduli by addition of Nd₂O₃ from 0 to 5.7 mol.
%

4. Conclusion

Analyses of the parameters (density, molar volume, elastic
moduli, and those theoretically acquired through the treat-
ment of longitudinal vibrations) were argued in terms of the
role of Nd₂O₃ that caused the formation of BO₄ increasing the
rigidity of glass respectively the glass density. The Nd³⁺ ions
affected the proportion of average bonds elongations to dimin-
ish from 48.18 % to reach the value of 45.59 % at 5.7 mol. % of
Nd₂O₃ which enhanced the elastic moduli of the glass system.

Conflicts of interest

The authors declare no conflicts of interest.

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