Bulgarian Chemical Communications, Volume 53, Issue 1 (pp. 18 - 25) 2021 *DOI: 10.34049/bcc.53.1.5172*

Correlations between optical characteristics and structure of sodium oxide-bismuth oxide-boron oxide glasses

T. R. Tasheva*, V. V. Dimitrov

Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., Sofia 1756, Bulgaria

Received: June 20, 2019; Revised: November 26, 2020

Glasses from the Na_2O-Bi_2O_3-B_2O_3 system were prepared using a conventional melt-quenching method. Oxide ion polarizability and optical basicity of the glasses were estimated. Both parameters were changed in a wide range (1.545-2.457 Å^3 for oxide ion polarizability and 0.589-0.990 for optical basicity). The theoretical refractive index was also determined and on its basis, the third-order nonlinear optical susceptibility $\chi^{(3)}$ was established by using generalized Miller's rule. Glasses possess comparatively high values for $\chi^{(3)}$ (0.90-2.42×10^{-13} esu). The structure of glasses was elucidated based on the interaction parameter, single bond strength, and IR spectral analysis. It was found that glasses with high Bi_2O_3 content possess low values for the interaction parameter (0.224-0.051 Å^{-3}) and low values for the single bond strength (377-198 kJ/mol) due to the presence of weak chemical bonds in the glass structure which were confirmed by IR spectral analysis. It was found that glasses with low Bi_2O_3 content were built-up by pyroborate and orthoborate groups, while those with high Bi_2O_3 content were built-up by orthoborate BO_3 groups linked with BiO_6 groups with mixed Bi-O-B bonds.

Keywords: borate glasses, bismuthate glasses, IR spectra, electronic polarizability, chemical bonding, nonlinear optical materials.

INTRODUCTION

In recent years attention of many researchers has been focused on exploring new functional materials with application in nonlinear optics. In this connection bismuth oxide (Bi_2O_3) based glasses are of great interest because of the high potential for application as photonic switches and THG (third-harmonic generation) materials due to high linear refractive index n_o and large third-order nonlinear optical susceptibility $\chi^{(3)}$ [1-3]. They are also promising candidates for broadband optical amplifiers and fiber laser applications [4]. Along with the excellent optical properties, the bismuthate glasses possess low melting temperatures, extensive glass formation range, and physical stability [5]. The Bi_2O_3-B_2O_3 binary system is a good example in this regard. During the years many studies on glass structure and optical properties have been carried out. For instance, data for refractive index and Abbe number, as well as data for density, glass transition temperature, and thermal expansion coefficient, have been reported by Ehrt [6]. The structure through ^{11}B MAS NMR and Raman spectroscopy, as well as the third-order nonlinear optical properties of Bi_2O_3-B_2O_3 glasses, have been examined by Terashima *et al.* [2]. Change of the boron coordination polyhedron from BO_3 to BO_4 has been proved. It has been found that the glasses exhibit large third-order nonlinear optical susceptibility $\chi^{(3)}$ of the order of 10^{-12} esu. Since the optical nonlinearity is caused by the electronic polarization of the glass upon exposure to intense light beams, polarizability is one of the most important properties which govern the nonlinearity response of the glass. The determination of electronic polarizability is the subject of the so-called polarizability approach which is well known in glass science [7-10]. The correlation between electronic polarizability, optical basicity, and XPS spectra of Bi_2O_3-B_2O_3 glasses has been studied by Honma *et al.* [11]. The glasses possess large electronic oxide ion polarizability and high optical basicity indicating their basic nature. The role of the single bond strength on the optical basicity of bismuth-borate glasses has been estimated by Dimitrov and Komatsu [12] and weak chemical bonds have been confirmed in the glass structure.

It is of scientific and practical interest to check the influence of a third oxide on the structure and optical properties of Bi_2O_3-B_2O_3 glasses. In this connection, the structure of ZnO-Bi_2O_3-B_2O_3 glasses and the role of the electronic oxide ion polarizability on the optical properties have been investigated by Inoue *et al.* [13] and Komatsu *et al.* [14]. Also, the polarizability approach has been applied and high third-order nonlinear optical properties have been predicted for TeO_2-Bi_2O_3-B_2O_3 glasses by Tasheva and Dimitrov [15].

* To whom all correspondence should be sent:
E-mail: tina.tasheva@gmail.com

The presence of weak chemical bonds between TeO_3, TeO_4, BiO_6, BO_3, and BO_4 groups has been confirmed by IR spectral analysis. According to Bishay and Maghrabi [16], a large range of glass formation exists in the Na_2O-Bi_2O_3-B_2O_3 system. In a recent review by Maeder [5] on bismuthate glasses, there is no evidence about the application of the polarizability approach for sodium oxide-bismuth oxide- boron oxide glasses. That is why the purpose of the present study was to synthesize Na_2O-Bi_2O_3-B_2O_3 glasses, to apply the polarizability approach to them, and to look for some relationships between the obtained polarizability parameters and the predicted third-order nonlinear optical susceptibility. The structure of the glasses in terms of IR-spectroscopy was also investigated.

EXPERIMENTAL

Four series with different compositions, Series A: (30-x)Na_2O.xBi_2O_3.70B_2O_3 (x=15, 20 and 25 mol%), Series B: (70-x)Na_2O.xBi_2O_3.30B_2O_3 (x=40, 50 and 60 mol%), Series C: (50-x)Na_2O.50Bi_2O_3.xB_2O_3 (x=45, 40, 35 and 30 mol%), Series D: (40-x)Na_2O.60Bi_2O_3.xB_2O_3 (x=35, 30, and 25 mol%) and glass with composition 5Na_2O.70Bi_2O_3.25B_2O_3 were prepared using a conventional melt-quenching method. The compositions of the obtained glasses are visualized in Figure 1.

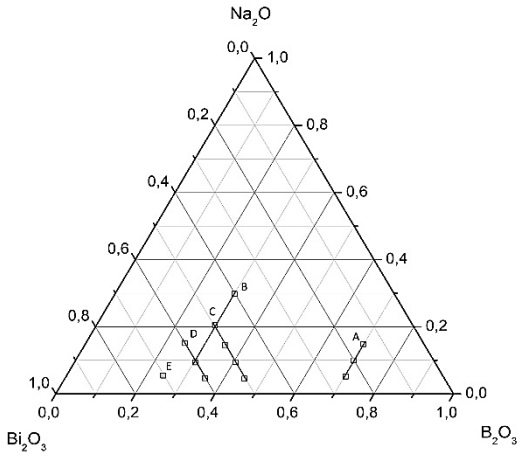

Fig. 1. Glass compositions in the Na_2O-Bi_2O_3-B_2O_3 ternary system.

Reagent-grade commercial powders of Bi_2O_3 (Alfa Aesar, 99%), H_3BO_3 (Alfa Aesar, 99.8%), and Na_2CO_3 (Sigma Aldrich, 99.8%) were mixed. Glasses from Series A were melted in porcelain crucibles at 850 °C for 20 min, and those from Series B, C, and D, as well as 5Na_2O.70Bi_2O_3.25B_2O_3, were melted in alumina crucibles at 900 °C for 20-30 min, depending on the composition, in an electric furnace. The melts were poured onto an alumina plate and pressed to a thickness of 1~2 mm by a copper plate. The experimental density was measured by the Archimedes method by using an analytical scale Mettler Toledo New Classic ME 104 equipped with a density kit. XRD analysis was carried out on a Bruker D8 Advance diffractometer (Germany), Cu K_α radiation. The IR spectra were recorded in KBr discs in the 2000 - 400 cm^{-1} range on the FT-IR spectrometer Varian 600-IR The precision of the absorption maxima was ±3 cm^{-1}.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The XRD patterns of 10Na_2O.20Bi_2O_3.70B_2O_3 and 10Na_2O.50Bi_2O_3.40B_2O_3 glasses are presented in Fig. 2. They prove the amorphous nature of the samples because no sharp peaks are observed in the whole range from 10 to 80° 2θ.

Electronic polarizability and optical basicity of glasses

The polarizability approach is based on the Lorentz-Lorenz equation which relates the molar refraction R_m to the refractive index n_0 and the molar volume V_m of the glass by:

$$R_m = \frac{(n_o{}^2-1)}{(n_o{}^2+2)} V_m = \frac{(n_o{}^2-1)}{(n_o{}^2+2)} \frac{M}{d} \quad (1)$$

where M is molar mass, and d is density.

Assuming that the molar refraction of the Na_2O-Bi_2O_3-B_2O_3 glasses is an additive quantity it follows that:

$$R_m = 2.52(x\alpha_{iNa^+} + y\alpha_{iBi^{3+}} + z\alpha_{iB^{3+}} + n\alpha_{O^{2-}}) \quad (2)$$

where α_{iNa^+}, $\alpha_{iBi^{3+}}$, and $\alpha_{iB^{3+}}$ are the polarizabilities of the cations Na^+, Bi^{3+}, and B^{3+}, $\alpha_{O^{2-}}$ is the polarizability of the oxide ion, *x, y,* and *z* are the numbers of the cations Na^+, Bi^{3+}, and B^{3+}, and *n* is the number of the oxide ions in one molecule of glass.

Duffy and Ingram [17, 18] proposed an approach for calculating the theoretical optical basicity and the electronic oxide ion polarizability of the glass based on the following equations:

$$\Lambda_{th} = X_1\Lambda_1 + X_2\Lambda_2 + X_3\Lambda_3 \quad (3)$$

and

$$a_{O^{2-}} = \frac{1.67}{1.67-\Lambda_{th}} \quad (4)$$

where X_1, X_2, X_3 are equivalent fractions based on the amount of oxygen each oxide contributes to the overall material stoichiometry and $\Lambda_1, \Lambda_2, \Lambda_3$ are basicities assigned to the individual oxides.

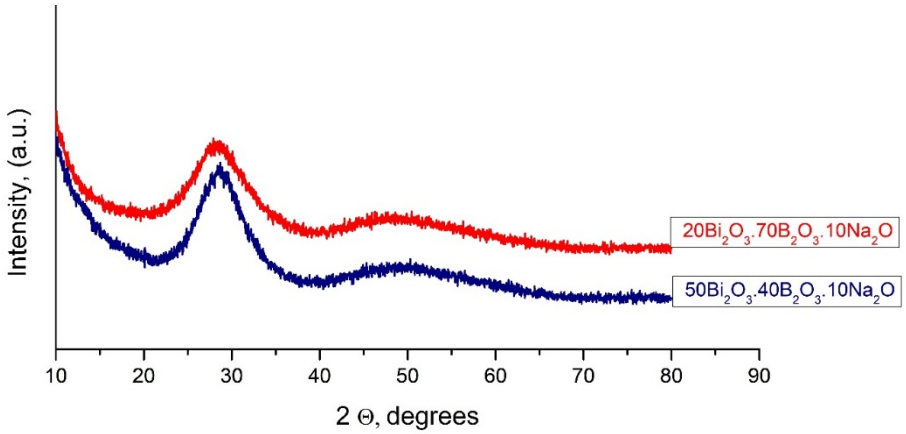

Fig. 2. XRD patterns of $10Na_2O.20Bi_2O_3.70B_2O_3$ and $10Na_2O.50Bi_2O_3.40B_2O_3$ glasses.

We calculated the theoretical optical basicity and oxide ion polarizability of Na_2O-Bi_2O_3-B_2O_3 glasses by Eqs. 3 and 4 using optical basicity data of Na_2O (Λ=1.15), Bi_2O_3 (Λ=1.19), and B_2O_3 (Λ=0.42) [8, 9, 17]. The molar refraction was calculated by Eq. 2 taking into account the cation polarizability and oxide ion polarizability. According to [8, 9] the cation polarizabilities are $\alpha_{Bi^{3+}}$= 1.508 Å^3; $\alpha_{B^{3+}}$= 0.002 Å^3, and $\alpha_{Na^{2+}}$= 0.175 Å^3. The molar volume was estimated based on the experimental data of density (Table 1). It should be noticed that our density data are in good agreement with the experimental data of binary Bi_2O_3-B_2O_3 glasses measured by Honma *et al.* [11], given in Table 1 in brackets. The obtained results of the optical basicity, oxide ion polarizability, and molar refraction are also presented in Table 1. As can be seen Λ_{th}, and $\alpha_{O^{2-}}$ are changed in a wide range (0.589-0.990 and 1.545-2.457 Å^3, respectively). Glasses with high Bi_2O_3 content possess the highest values for both parameters which indicates an increase in the basic nature of the glasses (0.911-0.990 and 2.199-2.457 Å^3, respectively).

Optical characteristics

According to the Lorentz-Lorentz equation, the refractive index n_0 could be expressed by:

$$n_0 = \sqrt{\frac{V_m+2R_m}{V_m-R_m}} \quad (5)$$

The refractive indices of Na_2O-Bi_2O_3-B_2O_3 glasses were calculated by us using equation 5 and the obtained results are presented in Table 2. It is seen that glasses possess comparatively high values in the 1.8 to 1.95 range. The refractive index increases with increasing Bi_2O_3 content. A comparison in Table 2 is given in brackets with experimental data for binary compositions reported by Honma *et al.* [11] which are very close to our results for the ternary system. This means that the prediction of the refractive index using the Lorentz-Lorentz equation is suitable.

The third-order nonlinear optical susceptibility $\chi^{(3)}$ can be predicted by generalizing the so-called Miller's rule:

$$\chi^{(3)} = [\chi^{(1)}]^4 . 10^{-10} \text{ , esu} \quad (6)$$

where $\chi^{(1)}$ is the linear optical susceptibility calculated by:

$$\chi^{(1)} = \frac{(n_o{}^2-1)}{4\pi} \quad (7)$$

We used the equations above to predict the third-order nonlinear optical properties of our glasses. The results are presented in Table 2. It is seen that glasses possess relatively high values for $\chi^{(3)}$ (1.00-2.45×10^{-13} esu). According to Terashima *et al.* [2, 19], the $\chi^{(3)}$ experimental values of Na_2O-B_2O_3 glasses are in the 0.324 - 0.658×10^{-13} esu range, while the $\chi^{(3)}$ values of binary Bi_2O_3-B_2O_3 glasses are in the 3.19 – 11.8×10^{-13} esu range. It is seen that the results in this study are close to those of Bi_2O_3-B_2O_3 glasses which means that the role of bismuth and boron oxide in our glasses is significant. Simultaneously, we have plotted the third-order nonlinear optical susceptibility as a function of the optical basicity of the glasses in Fig. 3. It is seen that optical nonlinearity increases with increasing the basic nature of the glasses, as well as glasses with increased Bi_2O_3 content, which possess the highest values for $\chi^{(3)}$, which means that glasses with increased electron donor ability possess higher values for the third-order nonlinear susceptibility.

Table 1. Series, compositions, molar mass M, density d, molar volume V_m, optical basicity Λ, oxide ion polarizability α_{O2-}, molar refraction R_m.

Series		Compositions			M, g/mol	d, g/cm^3	V_m, cm^3/mol	Λ	α_{O2-}, Å^3	R_m, cm^3/mol
		Na_2O	Bi_2O_3	B_2O_3						
Series A	A3	15	15	70	127.93	4.661	27.45	0.589	1.545	11.79
	A4	10	20	70	148.12	5.170	28.65	0.611	1.577	12.74
	A5	5	25	70	168.32	5.702	29.52	0.632	1.608	13.71
		(0)	(30)	(70)		(5.709)				
Series B	B4	30	40	30	225.86	5.800	38.94	0.896	2.158	16.36
	B5	20	50	30	266.26	6.375	41.77	0.920	2.228	18.58
	B6	10	60	30	306.66	7.105	43.16	0.941	2.291	20.82
Series C		(0)	(50)	(50)		(6.941)				
	C1	5	50	45	267.41	6.537	40.91	0.831	1.990	18.39
	C2	10	50	40	267.03	6.520	40.95	0.859	2.058	18.41
	C3	15	50	35	266.64	6.506	40.98	0.888	2.136	18.47
	C4/B5	20	50	30	266.26	6.375	41.77	0.920	2.228	18.58
Series D		(0)	(60)	(40)		(7.479)				
	D1	5	60	35	307.04	7.013	43.78	0.911	2.199	20.68
	D2/B6	10	60	30	306.66	7.105	43.16	0.941	2.291	20.82
	D3	15	60	25	306.28	6.700	45.71	0.974	2.399	21.02
	E1	5	70	25	346.68	7.159	48.43	0.990	2.457	23.32

Note: in brackets are given data according to Ref. 11.

Table 2. Series, compositions, refractive index n_0, third-order nonlinear optical susceptibility $\chi^{(3)}$, interaction parameter A, average single bond strength B_{M-O}

Series		Compositions			n_0	$\chi^{(3)}$. 10^{-13} esu	A, Å^{-3}	B_{M-O}, kJ/mol
		Na_2O	Bi_2O_3	B_2O_3				
Series A	A3	15	15	70	1.805	1.05	0.224	376.6
	A4	10	20	70	1.845	1.34	0.194	377.5
	A5	5	25	70	1.897	1.84	0.167	378.4
		(0)	(30)	(70)	(1.836)			
Series B	B4	30	40	30	1.781	0.90	0.132	215.6
	B5	20	50	30	1.845	1.34	0.098	217.5
	B6	10	60	30	1.948	2.45	0.072	219.3
		(0)	(50)	(50)	(2.074)			
Series C	C1	5	50	45	1.858	1.45	0.095	279.6
	C2	10	50	40	1.858	1.45	0.098	258.9
	C3	15	50	35	1.861	1.48	0.099	238.2
	C4/B5	20	50	30	1.845	1.34	0.098	217.5
Series D		(0)	(60)	(40)	(2.097)			
	D1	5	60	35	1.920	2.09	0.072	240.0
	D2/B6	10	60	30	1.948	2.45	0.072	219.3
	D3	15	60	25	1.855	1.71	0.071	198.6
	E1	5	70	25	1.946	2.42	0.051	200.5

Note: in brackets are given data according to Ref. 11.

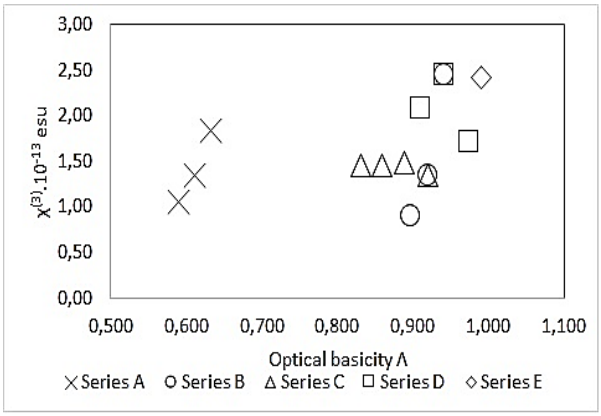

Fig. 3. Third-order nonlinear optical susceptibility as a function of optical basicity.

Chemical bonding of glasses

In the present communication, we applied two approaches proposed for estimation of the chemical bonding in simple oxides and ionic crystals, namely the thermodynamical approach by Sun [20] and the quantum-mechanical approach by Yamashita and Kurosawa [21]. Dimitrov and Komatsu [10, 22] adapted both approaches for the calculation of average single bond strength $B_{M\text{-}O}$ and interaction parameter A of oxide glasses. On this basis, in the case of our ternary oxide glasses we used the following equation for $B_{M\text{-}O}$:

$$B_{M-O} = xB_{Na-O}^{(6)} + yB_{Bi-O}^{(6)} + (1-x-y)B_{B-O}^{(3)} \quad (8)$$

where x, y, and (1-x-y) are molar parts of each oxide in the glass composition, and $B_{Na\text{-}O}$, $B_{Bi\text{-}O}$, and $B_{B\text{-}O}$ are 59 kJ/mol, 102.5 kJ/mol, and 498 kJ/mol, respectively, according to Refs. [12, 20].

The interaction parameter A of our ternary oxide glasses could be calculated by using the following equation:

$$A = X_{Na_2O}\frac{\left(3.921-\alpha_{O^{2-}}\right)}{2(\alpha_{iNa^+}+3.921)(\alpha_{O^{2-}}+\alpha_{iNa^+})} + X_{Bi_2O_3}\frac{\left(3.921-\alpha_{O^{2-}}\right)}{2(\alpha_{iBi^{3+}}+3.921)(\alpha_{O^{2-}}+\alpha_{iBi^{3+}})} + X_{B_2O_3}\frac{\left(3.921-\alpha_{O^{2-}}\right)}{2(\alpha_{iB^{3+}}+3.921)(\alpha_{O^{2-}}+\alpha_{iB^{3+}})} \quad (9)$$

where X_{Na2O}, X_{Bi2O3}, and X_{B2O3} are equivalent fractions based on the amount of oxygen each oxide contributes to the overall glass stoichiometry, $\alpha_{O^{2-}}$ is oxide ion polarizability of the glass and α_{iNa^+}, $\alpha_{iBi^{3+}}$, and $\alpha_{iB^{3+}}$ are cation polarizabilities of Na^+, Bi^{3+}, B^{3+}. Pauling's value of 3.921 $Å^3$ for the electronic polarizability of the free oxide ion is used.

We applied the equations above to our glasses and the results are presented in Table 2. The values for both parameters vary in a wide range (377 to 200 kJ/mol for $B_{M\text{-}O}$ and 0.224 to 0.051 $Å^{-3}$ for interaction parameter). It is seen that glasses with the highest values for A and $B_{M\text{-}O}$ are those with high boron content. On this basis, it should be noticed that glasses with the highest B_2O_3 content are built-up by strong predominantly covalent bonds, such as B-O-B. Such bonds were confirmed by Matsumoto *et al.* [23] based on the O1s XPS spectra of alkali borate and alkaline earth borate glasses. On the other hand, low values for A and $B_{M\text{-}O}$ suggest a small overlap between metal and oxide ions valence orbitals which leads to the presence of weak predominantly ionic bonds such as Bi-O-B and Bi-O-Bi which were proved by Honma *et al.* [11] using O1s XPS spectra of Bi_2O_3-B_2O_3 glasses. The third-order nonlinear optical susceptibility as a function of the interaction parameter is shown in Fig. 4. It is seen that the optical nonlinearity increases with decreasing the interaction parameter of the glasses.

IR spectral analysis

To confirm the presence of such bonds the structure of the glasses in the present study was investigated in terms of IR spectroscopy. The IR spectra of Na_2O-Bi_2O_3-B_2O_3 glasses are shown in Figs. 5 and 6. All spectra are characterized by four groups of well-defined bands in the following spectral ranges: at about 1400-1000 cm^{-1}, at around 900 cm^{-1}, 700 cm^{-1}, and 480 cm^{-1}.

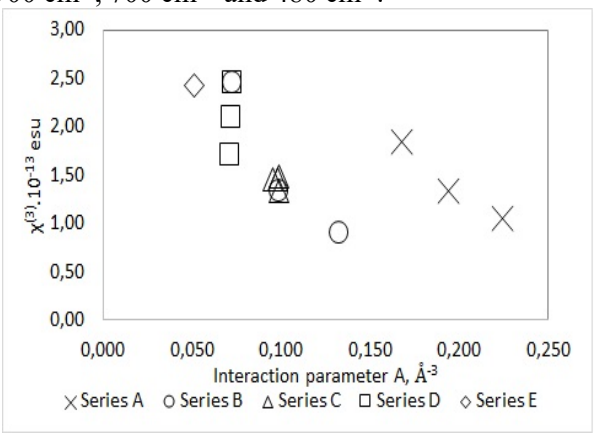

Fig. 4. Third-order nonlinear optical susceptibility as a function of the interaction parameter.

At the same time, it is seen that there is a strong increase in the intensity of the second (about 900 cm^{-1}) and fourth groups in the spectra (about 480 cm^{-1}) with increasing Bi_2O_3 content.

It is well known that the addition of a second oxide to B_2O_3 in oxide glasses leads to the transformation of BO_3 units to BO_4 units. This

change of coordination number of boron in Bi_2O_3 – B_2O_3 glasses has been studied by Terashima *et al*. [2] using ^{11}B MAS NMR spectroscopy. According to this study, the maximal concentration of BO_4 fractions (N_4) was found at about 30 mol% Bi_2O_3 and after that composition, a rapid decrease of N_4 fraction was observed.

The characteristic bands of boron-containing crystal and glasses are in the high-frequency range of the spectra in which are located the stretching vibrations of BO_3 and BO_4 structural units participating in different superstructural groups, namely pentaborate, diborate, pyroborate, and orthoborate groups. According to Plusnina [24], BO_3 group belongs to D_{3h} point group of symmetry and its vibrations in the spectra of borates are: double degenerate antisymmetric stretching vibration ν_d^s located at 1310-1000 cm^{-1}, symmetrical stretching vibration ν^s at 940-925 cm^{-1}, bending vibration δ at 725-765 cm^{-1} and doubly degenerate bending vibration δ_d at 680-590 cm^{-1}. According to the review study by Gautam *et al.* [25] on IR spectra of borate glasses, the antisymmetric stretching vibrations of B-O bonds of trigonal BO_3 units could be observed in the 1480-1200 cm^{-1} range. The band at about 1345-1235 cm^{-1} is connected with the presence of pyroborate and orthoborate groups, while the band at about 1235 cm^{-1} only to antisymmetric stretching vibrations of B-O bonds from orthoborate groups. The bands at about 1046-1020 cm^{-1} are assigned to the B-O stretching vibrations of BO_4 units. Thakur *et al*. [26] have reported that the peak at about 914 cm^{-1} can be described as the fundamental peak due to the B-O stretching vibrations accruing in the BO_4 units from diborate groups in the structure of Bi_2O_3-B_2O_3 glasses. Also, the peak at 1185 cm^{-1} can be attributed to antisymmetric stretching vibrations of B-O bonds of the BO_3 units from pyroborate and orthoborate groups.

On the other hand, according to IR spectral data of a large number of bismuthate crystals and glasses collected by Iordanova *et al*. [27] the stretching vibrations of BiO_6 units are in the 480-420 cm^{-1} range.

Based on the above discussion, the assignment of the bands in the spectra presented in Figs. 5 and 6 could be made. The bands at 1400-1100 cm^{-1} in the Series A and Series B glasses are connected with antisymmetric stretching vibrations of B-O bonds in BO_3 groups participating in pyroborate and orthoborate groups while the single band at about 1240 cm^{-1} in the spectra of the glasses of Series C and Series D is attributed to the same vibrations of BO_3 groups in orthoborate groups only. The shoulder at 1046 cm^{-1} in the spectra of Series A is assigned to stretching vibrations of BO_4 units, which probably participate in diborate structural groups.

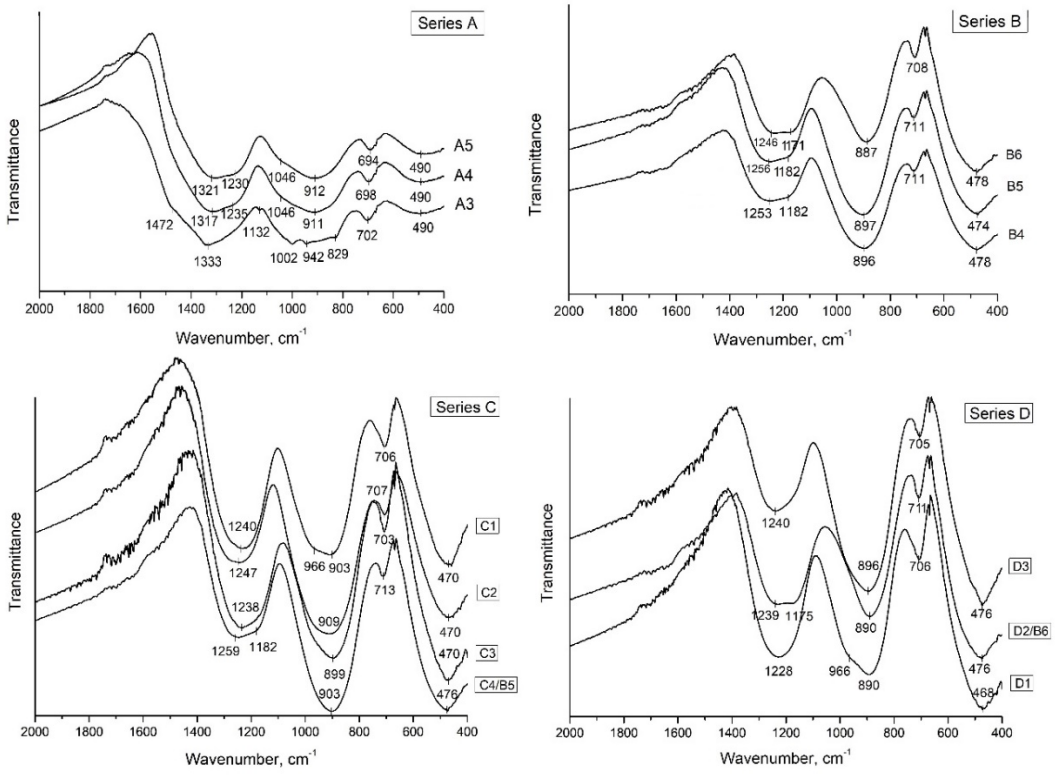

Fig. 5. IR spectra of Na_2O-Bi_2O_3-B_2O_3 glasses of Series A, Series B, Series C, Series D.

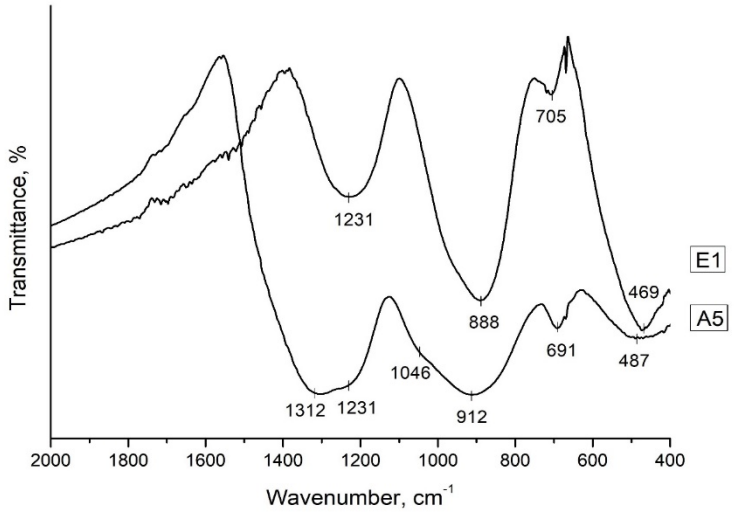

Fig. 6. IR spectra of Na_2O-Bi_2O_3-B_2O_3 glasses of $5Na_2O$-$25Bi_2O_3$-$70B_2O_3$ (A5) glasses and $5Na_2O$-$70Bi_2O_3$-$25B_2O_3$ glasses (E1).

The strong band at 470 - 490 cm^{-1} is attributed to the stretching vibrations of BiO_6 structural groups. The evidence of that is its intensity which increases with increasing Bi_2O_3 content.

The crystal structures of $2Bi_2O_3.B_2O_3$ compounds and orthoborate $BiBO_3$ have been investigated by Hyman and Perloff [28], and Becker and Fröhlich [29]. The structure of the first compound contains discrete planar BO_3 groups held together by coordination to BiO_6 groups. The structure of the second compound consists of $[Bi_2O_{10}]$ groups that are formed by two edge-sharing distorted $[BiO_6]$ octahedra. These groups are further sharing corners with planar BO_3 groups giving a three-dimensional framework. In both crystal structures, Bi-O-Bi and Bi-O-B bonds are formed. In this connection, the strong band at about 900 cm^{-1} in the spectra with high Bi_2O_3 content is probably due to similar BO_3 groups linked with BiO_6 octahedra with mixed Bi-O-B bonds. The increase in Bi_2O_3 content leads to increasing the number of such bonds in the structure which is responsible for the rapid increase of this band. A good example of such orthoborate glass compared with the IR spectrum of glass with a low Bi_2O_3 content is given in Fig. 6. The IR spectrum of $5Na_2O.70Bi_2O_3.30B_2O_3$ (E1) represents the spectrum of pure orthoborate glass built-up by isolated BO_3 groups connected with BiO_6 units.

Finally, the band at about 700 cm^{-1} could be assigned to the bending vibrations of borate groups.

Based on the structural analysis in this study presented above, the obtained low values of the average single bond strength B_{M-O} and the interaction parameter A of glasses with high Bi_2O_3 content, as well as the increase of the third-order nonlinear optical susceptibility $\chi^{(3)}$ (See Table 2 and Fig. 4) should be connected with the formation of Bi-O-Bi and Bi-O-B bonds with increased ionicity instead of strong covalent B-O-B bonds.

CONCLUSION

It was established that Na_2O-B_2O_3-B_2O_3 glasses with high Bi_2O_3 content possess high values of electronic oxide ion polarizability, refractive index, and third-order nonlinear optical susceptibility. The chemical bonding of the glasses was investigated by the interaction parameter, single bond strength, and IR spectroscopy. We found that glasses with low Bi_2O_3 content are built-up by pyroborate and orthoborate groups, while those with high Bi_2O_3 content are built-up by orthoborate BO_3 groups connected with BiO_6 groups with mixed Bi-O-B bonds between them.

Acknowledgements: *One of the authors (T. T.) would like to express her gratitude for providing her with financial support according to the National Program "Young scientists and postdoctoral students 2018/19" from the Ministry of Education and Science of the Republic of Bulgaria.*

REFERENCES

1. M. Yamane, Y. Asahara, Glasses for photonics, Cambridge University Press, 2000, p. 159.
2. K. Terashima, T. H. Shimoto, T. Yoko, *Phys. Chem. Glasses,* **38(4),** 211 (1997).
3. T. Hasegawa, T. Nagashima, N. Sugimoto, *Opt. Commun.,* **250**, 411 (2005).
4. S. N. Raju, C. A. Reddy, S. Sailaja, H. J. Seo, B. S. Reddy, *Luminescence,* **27**, 334 (2012).
5. T. Maeder, *Int. Mater. Rev.,* **58**, 3 (2013).
6. D. Ehrt, *Glass Technol.* **41**, 182 (2000).

7. W. A. Weyl, E. G. Marboe, The Constitution of Glasses, Wiley, New York, 1962.
8. V. Dimitrov, S. Sakka, *J. Appl. Phys.,* **79**, 1736 (1996).
9. V. Dimitrov, T. Komatsu, *Solid State Chem.,* **163**, 100 (2002).
10. V. Dimitrov, T. Komatsu, *J. Solid State Chem.,* **178**, 831 (2005).
11. T. Honma, Y. Benino, T. Komatsu, R. Sato, V. Dimitrov, *Phys. Chem. Glasses,* **43(1)**, 32 (2002).
12. V. Dimitrov, T. Komatsu, *J. Non-Cryst. Solids,* **382**, 18 (2013).
13. T. Inoue, T. Honma, V. Dimitrov, T. Komatsu, *J. Solid State Chem.,* **183**, 3078 (2010).
14. T. Komatsu, T. Inoue, T. Tasheva, T. Honma, V. Dimitrov, *J. Ceram. Soc. Japan,* **126(1)**, 8 (2018).
15. T. Tasheva, V. Dimitrov, *Bulg. Chem. Commun.,* **49(G)**, 43 (2017).
16. A. Bishay, C. Maghrabi, *Phys. Chem. Glasses,* **10(1)**, 1 (1969).
17. J. A. Duffy, M. D. Ingram, in: Optical Properties of Glass, D. Uhlman N. Kreidl (eds.), Am. Ceram. Soc., Westervill, 1991.
18. J. A. Duffy, *Phys. Chem. Glasses,* **30**, 1 (1989).
19. K. Terashima, S. H. Kim, T. Yoko, *J. Am. Ceram. Soc.,* **78(6)**, 1601 (1995).
20. K. H. Sun, *J. Am. Ceram. Soc.,* **30**, 277 (1947).
21. J. Yamashita, T. Kurosawa, *J. Phys. Soc. Japan,* **10**, 610 (1955).
22. V. Dimitrov, T. Komatsu, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol*. B, **46**, 521 (2005).
23. S. Matsumoto, Y. Miura, C. Murakami, T. Namba, *Proc. Second Int. Conf. on Borate Glasses, Crystals and Melts* 1997, A. C. Wright, S. A. Feller, A. C. Hannon (eds.), Society of Glass Technology, Sheffield, p. 112.
24. I. I. Plusnina, IR spectra of minerals, Moskwa, 1977 (in Russian).
25. C. Gautam, A. Kunar Yadav, A. Kunar Singh, *Int. Scholarly Res. Network* ISRN Ceramics, Article ID 428497 (2012).
26. S. Thakur, V. Thakur, A. Kaur, L. Singh, *J. Non-Cryst. Solids,* **512**, 60 (2019).
27. R. Iordanova, Y. Dimitriev, V. Dimitrov, S. Kassabov, D. Klissurski, *J. Non-Cryst. Solids,* **204**, 141 (1996).
28. A. Hyman, A. Perloff, *Acta Cryst.,* **B28**, 2007 (1972).
29. P. Becker, R. Fröhlich, *Z. Naturforsch.,* **59b,** 256 (2004).