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Synthesis, structure and nonlinear optical properties of tellurium oxide – bismuth oxide – boron oxide glasses

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TeO_2-Bi_2O_3-B_2O_3 glasses are prepared using a conventional melt-quenching method. The polarizability approach based on the Lorentz-Lorenz equation is applied and the optical basicity and the oxide ion polarizability are estimated. The glasses possess relatively high values of the optical basicity (0.734-0.936) and the electronic oxide ion polarizability (1.785-2.276 Å^3). The theoretical refractive index of the glasses is also estimated. On this basis the third order nonlinear optical susceptibility of the glasses is established using generalized Miller's rule. The glasses possess comparatively high third order nonlinear optical susceptibility in the 0.64-2.31x10^{-13} esu range. The chemical bonding of the glasses is elucidated on the basis of the interaction parameter and the single bond strength of an average cation-oxide ion (M-O) bond. It is found that the glasses possess relatively low values for the average single bond strength (352-254 kJ/mol) and low values of the interaction parameter (0.051-0.028 Å^{-3}). These results indicate for the presence of weak chemical bonds which are formed between TeO_4, TeO_3, BiO_6, BO_4 and BO_3 groups confirmed by IR spectral analysis.

Key words: *Oxide glasses, polarizability, optical basicity, chemical bonding, IR spectra, nonlinear optical materials*

INTRODUCTION

Nonlinear optical materials are attracted much attention because of their importance for the development of optical information processing technology. Since optical nonlinearity is caused by electronic polarization of a material upon exposure to intense light beams, the electronic polarizability is one of the most important properties which govern the nonlinear response of the material. The estimation of the electronic polarizability of ions is subject of the so called polarizability approach which is well known especially in the field of glass science [1]. During the past two decades numerous oxide glasses were investigated by means of the polarizability approach with aim to explain the origin of optical nonlinearity. It was established that bismuthate and tellurite glasses possess high optical nonlinearity and have possible application as nonlinear optical materials [2].

Tellurite glasses have attracted much scientific and practical attention due to their unique combination of properties such as low melting temperatures, chemical durability and stability, high dielectric constant, low phonon energy, broad optical transmission window and high linear and nonlinear refractive indices. In this respect TeO_2-based glasses are promising optical materials for up-conversion lasers and nonlinear optical materials exhibiting high second and third order nonlinear optical susceptibility [3-6].

Bismuthate glasses are of great interest also because of their potential for the application in the field of optoelectronics and nonlinear optics as photonic switches and third harmonic generation (THG) materials due to their low melting temperatures, extensive glass formation range, physical stability, high refractive index and high nonlinear optical susceptibility [7-9].

Recently, the optical properties and structure of TeO_2-Bi_2O_3-B_2O_3 glasses have been studied [10-12]. Hasegawa [10] has found that the glasses possess high refractive index, high optical basicity and high third order nonlinear optical susceptibility. Zhao *et al*. [11] have applied the polarizability approach and have investigated the structure of the glasses by means of Raman spectroscopy and XPS spectroscopy. Azuraida *et al*. [12] have made comparative studies of bismuth and barium boro-tellurite glasses and have concluded that the addition of Bi_2O_3 in boro-tellurite glasses improves the optical properties.

The purpose of the present study is to synthesis of novel TeO_2-Bi_2O_3-B_2O_3 glasses and to apply the polarizability approach to them. The structure of the glasses by means of IR-spectroscopy is also investigated.

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EXPERIMENTAL

Glasses in the ternary TeO_2-Bi_2O_3-B_2O_3 system were prepared using a conventional melt-quenching method. The glass compositions are given in Table 1, column 2. The compositions are divided into three series. Reagent grade commercial powders of TeO_2, Bi_2O_3 and H_3BO_3 were mixed together and melted in a corundum crucible at 900°C for 20 min in an electric furnace. The melts were poured onto an alumina plate and pressed to a thickness of 1~2 mm by another copper plate. The samples obtained from the third series of compositions were classified as opal glasses. The IR-spectra of the glasses were recorded in the 2000-400 cm^{-1} range by using FT-IR spectrometer Varian 600-IR. The samples for these measurements were prepared as KBr discs. The precision of the absorption maxima was ± 3 cm^{-1}.

THEORETICAL BACKGROUND

Recently, the polarizability approach has been applied to different simple oxides, binary and ternary oxide glasses [13-16]. The most familiar and widely used relationship in the polarizability approach is the Lorentz-Lorenz equation which relates the molar refraction (R_m) to the refractive index (n_o) and the molar volume (V_m) of the substance by,

$$R_m = \frac{\left(n_o^2 - 1\right)}{\left(n_o^2 + 2\right)} V_m \qquad (1)$$

Assuming that the molar refraction of a glass with a common molecular formula $A_xB_yC_zO_n$ is additive quantity it follows that,

$$R_m = 2.52(x\alpha_{iA} + y\alpha_{iB} + z\alpha_{iC} + n\alpha_{O^{2-}}) \qquad (2)$$

where $\alpha_{iA}, \alpha_{iB}, \alpha_{iC}$ are the polarizabilities of cations A, B and C and $\alpha_{O^{2-}}$ is the polarizability of the oxide ion, and *x*, *y* and *z* are the numbers of the cations A, B and C and *n* is the number of the oxide ions in one molecule of glass.

It is possible to calculate the so-called theoretical optical basicity Λ_{th} and the electronic oxide ion polarizability $\alpha_{O^{2-}}$ for ternary oxide glass on the basis of the following equations proposed by Duffy and Ingram [17,18],

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

and

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

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.

The third order nonlinear optical susceptibility $\chi^{(3)}$, can be predicted by generalized the so-called Miller’s rule [19],

$$\chi^{(3)} = [\chi^{(1)}]^4 .10^{-10} \text{ , esu} \qquad (5)$$

where $\chi^{(1)}$ is linear optical susceptibility calculated in accordance with,

$$\chi^{(1)} = \frac{\left(n_o^2 - 1\right)}{4\pi} \qquad (6)$$

Based on Sun’s fundamental condition of glass formation [20] Dimitrov and Komatsu [21] proposed an approach for calculation of average single bond strength B_{M-O} of oxide glasses using values of single bond strength B_{M-O} for corresponding simple oxides and taking into account the molar part of each oxide in the glass composition. In the case of ternary oxide glass the following equation can be used,

$$B_{M-O-} = xB_{A-O} + yB_{B-O} + \left(1 - x - y\right)B_{C-O} \qquad (7)$$

where x, y and (1-x-y) are molar parts of each oxide in the glass composition.

According to the general theory of the dielectric constant of simple ionic crystals based on quantum-mechanical treatment of the complex interaction between neighboring ions proposed by Yamashita and Kurosawa [22] the interaction parameter A of ternary oxide glass could be calculated by using the following equation [23],

$$A = X_1 \frac{\left(3.921 - \alpha_{O^{2-}}\right)}{2\left(\alpha_{iA} + 3.921\right)\left(\alpha_{O^{2-}} + \alpha_{iA}\right)} + X_2 \frac{\left(3.921 - \alpha_{O^{2-}}\right)}{2\left(\alpha_{iB} + 3.921\right)\left(\alpha_{O^{2-}} + \alpha_{iB}\right)} + X_3 \frac{\left(3.921 - \alpha_{O^{2-}}\right)}{2\left(\alpha_{iC} + 3.921\right)\left(\alpha_{O^{2-}} + \alpha_{iC}\right)} \qquad (8)$$

where X_1, X_2 and X_3 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_{iA}, α_{iB}, and α_{iC} are cation polarizabilities. Pauling’s value of 3.921 $Å^3$ for the electronic polarizability of the free oxide ion is used.

RESULTS AND DISCUSSION

We have calculated the theoretical optical basicity and oxide ion polarizability of TeO_2-Bi_2O_3-B_2O_3 glasses by Eq. 3 and 4 using optical basicity data of TeO_2 (Λ=0.975), Bi_2O_3 (Λ=1.19) and B_2O_3 (Λ=0.42) [23]. The molar refraction of the glasses was determined by Eq. 2 taking into account the cation polarizability and oxide ion polarizability. According to [13] the cation polarizabilities are $\alpha_{Te^{4+}}$ =1.595 $Å^3$; $\alpha_{Bi^{3+}}$ = 1.508 $Å^3$; $\alpha_{B^{3+}}$ = 0.002 $Å^3$.

Table 1 Composition, Molar mass M, density d, molar volume V_m, optical basicity Λ, electronic oxide ion polarizability $\alpha_{O^{2-}}$, molar refraction R_m

	Composition	**M, g/mol**	**d, g/cm^3**	**V_m, cm^3/mol**	**Λ**	**$\alpha_{O^{2-}}$, Å^3**	**R_m, cm^3/mol**
Series 1	$10TeO_{2}50\ Bi_{2}O_{3}40B_{2}O_{3}$	276.79	5.75	48.11	0.857	2.053	19.21
	$20TeO_{2}40Bi_{2}O_{3}40B_{2}O_{3}$	246.15	5.43	45.33	0.829	1.986	17.86
	$30TeO_{2}30Bi_{2}O_{3}40B_{2}O_{3}$	215.52	5.11	42.20	0.800	1.920	16.55
	$40TeO_{2}20Bi_{2}O_{3}40B_{2}O_{3}$	184.88	4.78	38.65	0.768	1.852	15.27
	$50TeO_{2}10Bi_{2}O_{3}40B_{2}O_{3}$	154.24	4.46	34.58	0.734	1.785	14.02
Series 2	$45.5\ TeO_{2}30.0Bi_{2}O_{3}24.5B_{2}O_{3}$	256.05	5.85	43.76	0.891	2.143	18.83
	$59.65TeO_{2}25.0Bi_{2}O_{3}15.35B_{2}O_{3}$	222.38	5.89	37.76	0.936	2.274	18.08
	$60.2TeO_{2}20.0Bi_{2}O_{3}19.8B_{2}O_{3}$	203.06	5.56	36.54	0.891	2.145	16.90
Series 3	$31.2TeO_{2}45.0\ Bi_{2}O_{3}23.8B_{2}O_{3}$	276.05	6.21	44.44	0.936	2.274	20.08
	$31.0TeO_{2}40.0Bi_{2}O_{3}29.0B_{2}O_{3}$	229.46	5.70	40.25	0.891	2.145	17.86
	$45.5TeO_{2}35.0\ Bi_{2}O_{3}19.5B_{2}O_{3}$	249.28	6.05	41.18	0.936	2.276	19.09

The molar volume was estimated and the results of V_m, theoretical optical basicity Λ_{th}, oxide ion polarizability $\alpha_{O^{2-}}$ and molar refraction R_m are listed in Table 1. It is seen that the glasses possess relatively high optical basicity (0.734-0.936) and electronic oxide ion polarizability (1.785 - 2.276 Å^3) which indicate for their basic nature. The results obtained are in good agreement with the data reported by Hasegawa [10] and Zhao *et al.* [11] for other bismuth boro-tellurite glasses. We have estimated the theoretical refractive index of TeO_2-Bi_2O_3-B_2O_3 glasses using Eq. 1. The data are listed in Table 2, column 3. As can be seen the glasses possess high values of refractive index in the 1.713-1.938 range. The third order nonlinear optical susceptibility $\chi^{(3)}$, was predicted by generalized Miller's rule (see Eqs. 5 and 6). The results are listed in Table 2, column 4. TeO_2-Bi_2O_3-B_2O_3 glasses show relatively high values of the third order nonlinear optical susceptibility in the 0.64-2.31 x 10^{-13} esu range which are close to those reported in Refs. 24, 25. This means that TeO_2-Bi_2O_3-B_2O_3 glasses are probably good candidates for nonlinear optical applications. It was established that third order nonlinear optical susceptibility $\chi^{(3)}$ of the glasses increases with increasing electronic oxide ion polarizability, that is optical basicity and refractive index.

As can be seen in Table 1 the glasses with high optical nonlinearity possess high electronic oxide ion polarizability, optical basicity and refractive index.

Sun [20] has suggested a bond energy criterion for glass formation and has reported comprehensive data on single bond strength B_{M-O} in kcal per Avogadro bond for various simple oxides based on their dissociation energy E_d. Yamashita and Kurosawa [22] have proposed a general theory of the dielectric constant of simple ionic crystals based on quantum-mechanical treatment of the electronic structure of constituent ions in order to take into account the effect of charge overlapping between neighboring ions.

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

	Composition	n_0	$X^{(3)}.10^{-13}$ esu	A, Å^{-3}	B_{M-O}, kJ/mol
Series 1	$10TeO_{2}50\ Bi_{2}O_{3}40B_{2}O_{3}$	1.730	0.64	0.036	279
	$20TeO_{2}40Bi_{2}O_{3}40B_{2}O_{3}$	1.718	0.58	0.039	297
	$30TeO_{2}30Bi_{2}O_{3}40B_{2}O_{3}$	1.713	0.56	0.042	316
	$40TeO_{2}20Bi_{2}O_{3}40B_{2}O_{3}$	1.720	0.59	0.046	334
	$50TeO_{2}10Bi_{2}O_{3}40B_{2}O_{3}$	1.745	0.70	0.051	352
Series 2	$45.5\ TeO_{2}30Bi_{2}O_{3}24.5B_{2}O_{3}$	1.807	1.06	0.033	283
	$59.65TeO_{2}25.0Bi_{2}O_{3}15.35B_{2}O_{3}$	1.938	2.31	0.028	272
	$60.2TeO_{2}20Bi_{2}O_{3}19.8B_{2}O_{3}$	1.893	1.79	0.033	291
Series 3	$31.2TeO_{2}45.0\ Bi_{2}O_{3}23.8B_{2}O_{3}$	1.864	1.50	0.028	254
	$31.0TeO_{2}40Bi_{2}O_{3}29.0B_{2}O_{3}$	1.842	1.32	0.032	274
	$45.5TeO_{2}35.0\ Bi_{2}O_{3}19.5B_{2}O_{3}$	1.895	1.81	0.028	263

A quantitative measure of this complex interaction is given by the so-called interaction parameter *A*, which in fact for a chosen cation-anion pair represents the charge overlapping of the oxide ion with its nearest positive neighbor. Therefore, the average single bond strength and the interaction parameter represent the chemical bonding of the glasses based on two different approaches – on the thermodynamics and polarizability, respectively. Both parameters of TeO_2-Bi_2O_3-B_2O_3 glasses were estimated by using Eqs. 7 and 8. For the calculation of the average single bond strength of the glasses the following values for the corresponding individual oxides were used - 285 kJ/mol for TeO_2, 103 kJ/mol for Bi_2O_3 and 498 kJ/mol for B_2O_3 (see Ref. 23). The obtained data for both parameters are presented in Table 2. The glasses possess small single bond strength in the 254-352 kJ/mol range and small values of interaction parameter in the 0.028-0.051 $Å^{-3}$ range. Small interaction parameter means week interionic interactions resulting in large unshared electron density at one averaged oxide ion. These values of B_{M-O} and A suggest for the presence of predominantly ionic character of the bonds in the glass structure. Probably Te-O-B, Te-O-Bi and Te-O-Te, along with Bi-O-B and Bi-O-Bi chemical bonds are formed in their structure.

With a view to confirm the presence of such bonds the structure of the glasses in the present study was investigated by means of IR spectroscopy. The IR spectra of TeO_2-Bi_2O_3-B_2O_3 glasses are shown in Figs. 1-3. In the spectra of the glasses from Series 1 (Fig. 1) it can be seen the presence of two well-defined bands at 1338-1164 cm^{-1} range, a band at 1014-1001 cm^{-1} and two low frequency bands at about 670 cm^{-1} and 440 cm^{-1}. The intensity of the band at about 670 cm^{-1} increases and that of the band at about 440 cm^{-1} decreases with the TeO_2 content increase and Bi_2O_3 content decrease.

In the spectra of the glasses from Series 2 (Fig. 2) it can be seen the presence of two well-defined maxima at 1325-1316 cm^{-1} and 1210-1206 cm^{-1} respectively, weak maxima at 1071-1017 cm^{-1} and strong band at about 658-649 cm^{-1} with a shoulder at 750-742 cm^{-1} .

The spectra of the glasses from Series 3 are similar each other. A broad band in the 1325-1206 cm^{-1} could be observed along with weak band at around 1045-1022 cm^{-1} in the high frequency range. In the low frequency range four or five bands exist, namely at 759-713 cm^{-1} , 658-633cm^{-1} , 617 cm^{-1} , 562-548 cm^{-1} and 438-433 cm^{-1}. The last band decreases its intensity with Bi_2O_3 decrease.

The change of the tellurium coordination polyhedron from TeO_4 to TeO_3, the change of boron coordination polyhedron from BO_3 to BO_4 and existence of BiO_6 and BiO_3 groups are well known from structural investigations of different tellurite, borate and bismuthate glasses [7, 25-30]. Arnaudov *et al*. [26] and Dimitriev *et al*. [27] have studied the Te-O stretching vibrations of α-TeO_2 and 16 crystalline tellurites built up by TeO_3, TeO_4 or combinations of these polyhedra as well as series of tellurite glasses containing similar polyhedra. The characteristic stretching vibrations of these structural groups are located in the 670-635 cm^{-1} range. According to IR- spectral data for large number of bismuthate crystals and glasses collected by Iordanova *et al*. [30] the stretching vibrations of BiO_6 are in the 480-420 cm^{-1} range while those of BiO_3 groups are around 860-840 cm^{-1}.

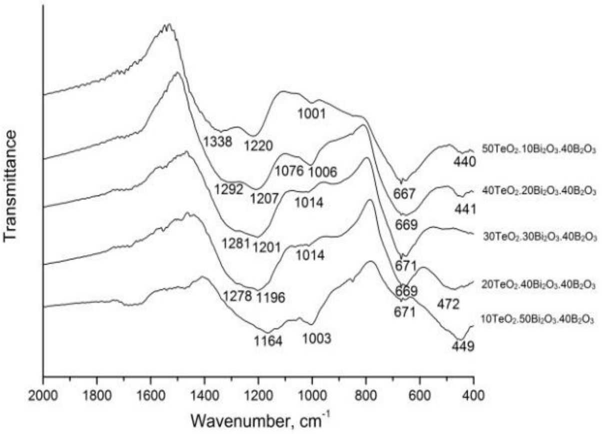

Fig. 1. IR spectra of the TeO_2-Bi_2O_3-B_2O_3 glasses from Series 1.

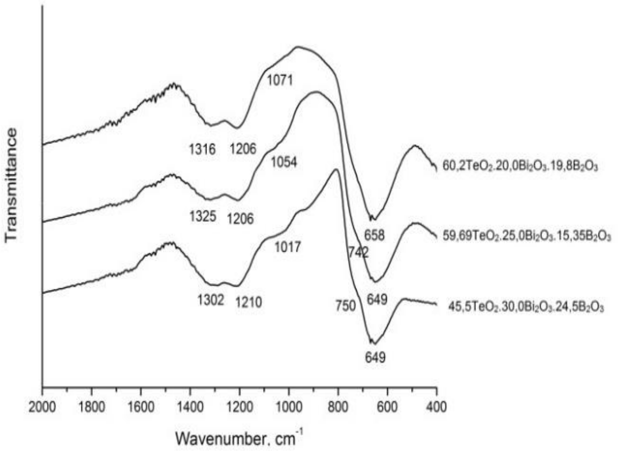

Fig. 2. IR spectra of the TeO_2-Bi_2O_3-B_2O_3 glasses from Series 2.

The characteristic bands of boron containing crystals 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 groups.

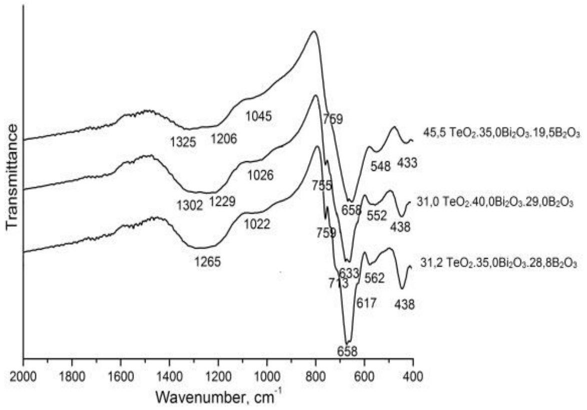

Fig. 3. IR spectra of the TeO_2-Bi_2O_3-B_2O_3 glasses from Series 3.

According to the review article by Gautam *et al.* [31] on infrared spectroscopic studies of borate glasses with different additives the asymmetric 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. The absorption maxima at about 1015 cm^{-1} gives information of the presence of pentaborate groups containing both BO_3 and BO_4 units. The bonds at about 1046-1020 cm^{-1} are assigned to the B-O stretching vibrations of BO_4 units. Similar results about the vibrations of BO_3 and BO_4 units in the structure ZnO-Bi_2O_3-B_2O_3 and CdO-Bi_2O_3-B_2O_3 have been reported also by Saritha *et al.* [32] and Pal *et al.* [33].

On the basis of the discussion mentioned above the following assignment of the bands in the spectra of TeO_2-Bi_2O_3-B_2O_3 glasses is made. The bands in the 1338-1278 cm^{-1} range and the bands at 1229-1196 cm^{-1} range are assigned to the asymmetrical stretching vibrations of BO_3 units in pyro- and orthoborate superstructural units. The absorption maxima in the 1071-1001 cm^{-1} range is attributed to the stretching vibrations of BO_4 units. The absorption band around 670-650 cm^{-1} is probably due to overlapping between asymmetrical stretching vibrations of axial Te-O bonds in the TeO_4 groups and asymmetrical stretching vibrations of TeO_3 pyramidal groups. The shoulder at 760-713 cm^{-1} could be assigned to symmetrical stretching vibrations of equatorial Te-O bonds in TeO_4 groups or to symmetrical stretching vibrations of TeO_3 groups. The band around 440 cm^{-1} is attributed to the Bi-O stretching vibrations of BiO_6. The observed structural units namely BO_3, BO_4, TeO_3, TeO_4 and BiO_6 are interconnected in the structure of the TeO_2-Bi_2O_3-B_2O_3 glasses by B-O-B, B-O-Te, B-O-Bi, Te-O-Te and Bi-O-Bi chemical bonds.

CONCLUSION

The polarizability approach based on the Lorentz-Lorenz equation has been applied to TeO_2-Bi_2O_3-B_2O_3 glasses. It was established that the glasses possess high refractive index (1.713-1.938), high electronic ion polarizability (1.785-2.276 $Å^3$) and high optical basicity (0.734-0.936). The theoretical third order nonlinear optical susceptibility $\chi^{(3)}$ was determined and it was found that the glasses possess high values of $\chi^{(3)}$ in the $0.64\text{-}2.31 \times 10^{-13}$ range. It was established that the glasses have small single bond strength and interaction parameter, thus suggesting the presence of weak chemical bonds. Such bonds, namely B-O-Te, B-O-Bi, Te-O-Te and Bi-O-Bi probably interconnect TeO_4, TeO_3, BiO_6, BO_3 and BO_4 groups which were confirmed by IR spectral analysis of the glasses. The high polarizability of oxide ions in these bonds accounts to the observed linear and nonlinear optical properties of the glasses.

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СИНТЕЗ, СТРУКТУРА И НЕЛИНЕЙНИ ОПТИЧНИ СВОЙСТВА НА ТЕЛУР-БИСМУТ-БОР ОКСИДНИ СТЪКЛА

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(Резюме)

TeO_2-Bi_2O_3-B_2O_3 стъкла бяха синтезирани посредством рязко охлаждане на стопилки. Беше приложен поляризационния подход, базиран на уравнението на Лорентц-Лоренц. Оптическата основност и кислородната поляризуемост бяха определени. Установено е, че стъклата притежават сравнително високи стойности за оптическата основност (0.734-0.936) и кислородната електронна поляризуемост (1.785-2.276 Å^3). Теоретичният показател на пречупване също беше определен. На негова основа беше определена нелинейната оптическа възприемчивост от трети порядък $\chi^{(3)}$ посредством Милеровото правило. Стъклата притежават сравнително високи стойности за $\chi^{(3)}$ (0.64-2.31x10^{-13} esu). Химическото свързване е изяснено, на основата на една осреднена катион-кислород (M-O) химична връзка, посредством параметъра на междуйонно взаимодействие и здравината на връзката. Установено е, че стъклата притежават сравнително ниски стойности за здравината на химичната връзка (352-254 kJ/mol) и ниски стойности за параметъра на междуйонно взаимодействие (0.051 до 0.028 Å^{-3}), Тези резултати предполагат наличието на слаби химични връзки между TeO_4, TeO_3, BiO_6, BO_4 и BO_3 групите, потвърдени чрез ИЧ спектрален анализ.

Ключови думи: *оксидни стъкла, поляризуемост, оптическа основност, химическо свързване, ИЧ спектроскопия, нелинейни оптични материали.*