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Electronic polarizability, optical basicity and chemical bonding of zinc oxide-barium oxide-vanadium oxide glasses

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Glasses with compositions $xZnO.(35-x)BaO.65V_2O_5$ (x= 1, 3, 5, 7, 10, 15 and 20 mol%) were prepared using a conventional melt quenching method. XRD, DTA and DSC analysis were performed. The results of XRD analysis confirm amorphous nature of the samples. The ternary glasses possess low glass transition temperatures T_g and crystallization temperatures T_x. The measured density decreases with increase of ZnO content from 3.974 g/cm^3 to 3.245 g/cm^3. The theoretical refractive index, electronic oxide ion polarizability and optical basicity of the glasses were calculated by Lorentz-Lorenz equation. The glasses were found to possess high refractive index (2.112-2.421), high electronic oxide ion polarizability (2.692-2.725 Å^3) and high optical basicity (1.050-1.057). The third order nonlinear optical susceptibility $\chi^{(3)}$ was determined by generalized Miller's rule. It was established that $\chi^{(3)}$ is high in the 0.58-2.24x10^{-12} esu range. The average single bond strength B_{M-O} and interaction parameter $A(n_o)$ were calculated. The bond strength was found to vary from 251 to 253 kJ/mol and interaction parameter was in the 0.049-0.053 Å^{-3} range, thus suggesting the presence of weak chemical bonds. Such bonds, namely Ba···O=V, V-NBO (nonbridging oxygen), V-O-Zn and V-O-V were confirmed by IR-spectra of the glasses. The high polarizability of the oxide ions in these bonds accounts for the observed linear and nonlinear optical properties of the glasses. A structural model of glasses containing VO_5, VO_4 and ZnO_4 groups is proposed.

Keywords: oxide glasses, refractive index, electronic polarizability, optical basicity, chemical bonding, IR spectra, nonlinear optical materials

INTRODUCTION

One of the most important properties of materials, which is closely related to their applicability in the field of optics and electronics, is the electronic polarizability of ions. It demonstrates the ease of deformation of their electronic clouds by the application of an electromagnetic field. It is closely related to interionic interactions as well as to many properties of the materials such as refraction, conductivity, electro-optical effect, ferroelectricity, optical basicity along with optical nonlinearity [1-4]. An estimate of the state of polarization of ions is obtained using the so-called polarizability approach based on the Lorentz-Lorenz equation [5]. The polarizability approach was systematically developed in our recent investigations concerning the origin of electronic ion polarizability and optical basicity of numerous simple oxides and oxide glasses [6-8].

According to the pioneering studies of Duffy and Ingram [9], the bulk optical basicity, Λ, of an oxide medium is a numerical expression of the average electron donor power of the oxide species constituting the medium and can be a measure of the acid-base properties of oxides, glasses, alloys, slags, molten salts, etc.

V_2O_5 containing oxide glasses are non-conventional group vitreous materials and their electronic conductivity and semiconducting properties are well known [10, 11]. Recently, the optical properties of vanadate glasses have attracted much attention because of possible application in the field of nonlinear optics. The nonlinear optical properties of V_2O_5 thin film and TeO_2-V_2O_5 bulk glasses have been investigated and high values of the third order nonlinear optical susceptibility $\chi^{(3)}$ have been obtained [12, 13]. Also recently, $\chi^{(3)}$ of BaO-V_2O_5, Fe_2O_3-BaO-V_2O_5, B_2O_3-BaO-V_2O_5 and TiO_2-BaO-V_2O_5 glasses has been predicted [14-16]. The obtained values of $\chi^{(3)}$ based on experimental data and predicted data are rather large, indicating that such glasses are interesting materials for non-linear optical devices.

On the other hand ZnO possess interesting mechanical, thermal, electrical and optical properties. That is why today ZnO-based materials and devices including magnetic semiconductors, light emitting devices, photodiodes, metal-isulator-semiconductors, transparent thin-film transistors and nanostructures are very attractive [17]. Simultaneously, the oxide glasses containing high ZnO content seem also promising materials from

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optical nonlinearity point of view. For example, Ticha et al. have reported high values of nonlinear refractive index for PbO-ZnO-P_2O_5 glasses [18]. Recently, Zawadzka et al. have measured second and third harmonic generation of ZnO thin film for NLO applications and obtained high values for nonlinear optical susceptibility [19].

That is why it is of scientific and practical interest to check the together influence of V_2O_5 and ZnO on the optical properties of the glasses. In this connection the purpose of the present study is to investigate the electronic oxide ion polarizability that is optical basicity, interaction parameter and average single bond strength of ZnO-BaO-V_2O_5 glasses and have looked for some intrinsic relationship between them and predicted third order nonlinear optical susceptibility. The correlation with the structure of the glasses has been also estimated.

EXPERIMENTAL

Glasses with composition of xZnO.(35-x)BaO.65V_2O_5 (x= 1, 3, 5, 7, 10, 15 and 20 mol %) were prepared by using a conventional melt-quenching method. Chemical powders of reagent grade ZnO, V_2O_5 and $BaCO_3$ were mixed together and melted in a porcelain crucible at 900 – 950℃ in an electric furnace for 15 min. The melts were poured onto an aluminum plate and pressed to thickness of 1-2 mm by another copper plate.

Densities of the glasses at room temperature were determined by pycnometer using distilled water as immersion liquid. The IR-spectra of 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}. DSC curves were made at 10 ℃/min using STA PT 1600 TG-DTA/DSC LINSEIS Messgerate GmbH calorimeter. The glass transition temperature T_g and crystallization temperature T_x were estimated from the DSC curves. The amorphous nature of the samples was identified using X-Ray diffractometer Philips APD15 Cu k_α graphite monochromator.

RESULTS AND DISCUSSION

Density, X-ray diffraction and DSC/DTA analysis

The obtained results of the density of the glass samples are presented at Table 1, column 2. As can be seen with increasing ZnO content the density decrease from 3.974-3.245 g/cm^3.

X-ray diffraction investigation of the studied glasses reveals no diffraction peaks and the results indicate that the prepared samples were of high quality glasses. An example of X-ray diffraction pattern of 5ZnO.30.BaO.65V_2O_5 glass is presented in Fig. 1.

The values and compositional dependence of the glass transition temperature T_g and the crystallization temperature T_x of ZnO-BaO-V_2O_5 glasses were similar to each other. The glasses possess low glass transition temperatures T_g of 262º – 303 ºC and crystallization temperatures T_x of 315º – 372ºC. For example the DTA and DSC curves of glass with composition 5ZnO.30BaO.65V_2O_5 are shown in Fig. 2. As can be seen T_g is 299 ºC and sharp exo effect corresponding to Tx exist at 372 ºC. At the same time the difference $\Delta T = T_x - T_g$ is small in the 50 - 73 ºC range which indicates for low thermal stability of ZnO -BaO-V_2O_5 glasses. Recently, similar results were obtained for B_2O_3-BaO-V_2O_5 and TiO_2-BaO-V_2O_5 glasses [15,16].

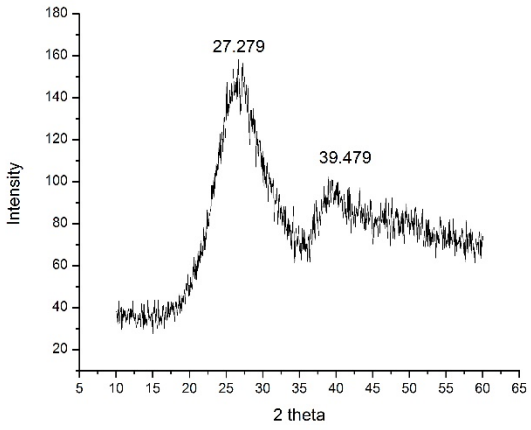

Fig. 1. XRD pattern of glass with composition 5ZnO.30BaO.65V_2O_5.

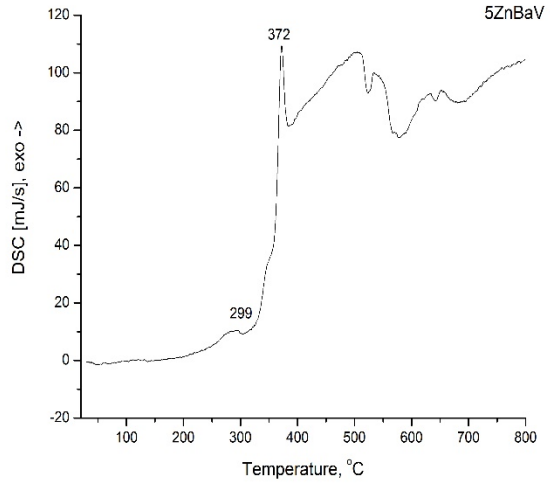

Fig. 2. DSC curve of glass with composition 5ZnO.30BaO.65V_2O_5.

Table 1. Composition, density d, molar mass M, molar volume V_m , optical basicity Λ_{th}, electronic oxide ion polarizability αo^{2-} and molar refractivity R_m of ZnO-BaO-V_2O_5 glasses

Composition	d, g/cm^3	M, g/mol	V_m	Λ_{th}	αo^{2-}, Å^3	R_m
1ZnO.34BaO.65V_2O_5	3.974	171.17	43.07	1.057	2.725	26.63
3ZnO.32BaO.65V_2O_5	3.928	169.73	43.21	1.056	2.721	26.56
5ZnO.30BaO.65V_2O_5	3.852	168.29	43.69	1.056	2.718	26.50
7ZnO.28BaO.65V_2O_5	3.591	166.86	46.47	1.055	2.714	26.43
10ZnO.25BaO.65V_2O_5	3.415	164.70	48.23	1.054	2.709	26.33
15ZnO.20BaO.65V_2O_5	3.337	161.10	48.28	1.052	2.701	26.17
20ZnO.15BaO.65V_2O_5	3.245	157.51	48.54	1.050	2.692	26.00

Application of polarizability approach to ZnO-BaO-V_2O_5 glasses

Electronic polarizability and optical basicity of ZnO-BaO-V_2O_5 glasses

Determination of electronic oxide ion polarizability is an object of so called polarizability approach. Polarizability approach in glass science is based on the Lorentz-Lorenz equation which relates molar refraction R_m to refractive index n_o and molar volume V_m of the substance by,

$$\boldsymbol{R_m = \frac{{n_0}^2-1}{{n_0}^2+2}.V_m} \quad (1)$$

This equation gives the average molar refraction of isotropic substances, i.e., for liquids, glasses and cubic crystals. R_m can be expressed as a function of molar polarizability α_m. With α_m in (Å^3) the following equation can be used,

$$R_m = 2.52\alpha_m \quad (2)$$

Assuming that molar polarizability α_m of a glass is additive quantity, it follows that for ternary oxide glass with general molar formula xZnO.(0,35-x)BaO.0,65V_2O_5 the molar refraction could be presented as follows,

$$R_m = 2.52(\sum\alpha_i + N\alpha_{O^{2-}}) = 2.52\ (a.\alpha_{Zn^{2+}} + b.\alpha_{Ba^{2+}} + c.\alpha_{V^{5+}} + N.\alpha_{O^{2-}}) \quad (3)$$

where $\sum\alpha_i$ denotes molar cation polarizability, $\alpha_{Zn^{2+}}$, $\alpha_{Ba^{2+}}$ and $\alpha_{V^{5+}}$ are cation polarizabilities of Zn^{2+} , Ba^{2+} and V^{5+} respectively, $\alpha_{O^{2-}}$is electronic oxide ion polarizability, *a, b, c* are numbers of cations and *N* is number of oxide ions in one molecule of glass. According to [6] the cation polarizabilities are: $\alpha_{Zn^{2+}}$ = 0.283 Å^3 ; $\alpha_{Ba^{2+}}$= 1.595 Å^3 ; $\alpha_{V^{5+}}$ = 0.122 Å^3.

The electronic oxide ion polarizability $\alpha_{O^{2-}}$ which participate in Eq. 3 we have calculated from theoretical optical basicity Λ_{th} of ZnO-BaO-V_2O_5 glasses in accordance with the approach proposed by Duffy and Ingram [20]:

$$\Lambda_{th} = X_{ZnO}\Lambda_{ZnO} + X_{BaO}\Lambda_{BaO} + X_{V_2O_5}\Lambda_{V_2O_5}, \quad (4)$$

where X_{ZnO}, $X_{BaO}$and $X_{V_2O_5}$ are equivalent fractions based on the amount of oxygen contributed by each oxide to the overall glass stoichiometry, Λ_{ZnO}, Λ_{BaO} and $\Lambda_{V_2O_5}$ are optical basicities of individual oxides (Λ_{ZnO}=1.08; Λ_{BaO}=1.22 and $\Lambda_{V_2O_5}$=1.04 [7,21]).

On the basis of an intrinsic relationship between electronic polarizability of the oxide ions $\alpha_{O^{2-}}$ and optical basicity of the oxide medium Λ, proposed by Duffy [22] the oxide ion polarizability can be calculated by using this equation:

$$\alpha_{O^{2-}} = \frac{1,67}{1,67-\Lambda} \quad (5)$$

Using the obtained basicity data with Eq. (4) the oxide ion polarizability $\alpha_{O^{2-}}$ of ZnO-BaO-V_2O_5 glasses was determined my means of Eq. (5). On the basis of the data for oxide ion polarizability the molar refraction R_m of the glasses was calculated using Eq. (3). The molar volume V_m was estimated on the basis of the molar mass and density of the glasses. The data for molar volume 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 high optical basicity (~1) and high electronic oxide ion polarizability (2.725 - 2.692 Å^3) which indicate for their basic nature.

Refractive index of ZnO-BaO-V_2O_5 glasses

According to the Lorentz-Lorenz equation the refractive index n_o of the substance can be presented as,

$$n_0 = \sqrt{\frac{V_m+2R_m}{V_m-R_m}} \quad (6)$$

We have estimated the theoretical refractive index of ZnO-BaO-V_2O_5 glasses using Eq. 6. The data are listed in Table 2, column 2. As can be seen the glasses possess high values of refractive index in the 2.421-2.112 range. The results shown in Table 2 are in good agreement with experimental data for refractive index of thin films of V_2O_5 (n_o=2.59) [12] as well as crystalline ZnO (n_o=2.008) [6].

Chemical bonding of the glasses

Average single bond strength of the glasses

Based on Sun's fundamental condition of glass formation [23] Dimitrov and Komatsu [24] 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. The bond strength of different glasses such as phosphate, silicate, germanate, tellurite and bismuthate glasses has been estimated [24, 25]. In the case of ZnO-BaO-V_2O_5 glasses the following equation can be used,

$$B_{M-O} = xB_{Zn-O} + yB_{Ba-O} + (1-x-y)\,B_{V-O} \quad (7)$$

where B_{Zn-O}, B_{Ba-O} and B_{V-O} are single bond strength of M-O in the corresponding individual oxide (138 kJ/mol for BaO, 151 kJ/mol for ZnO and 313 kJ/mol for V_2O_5 (see Ref. 26)). We have determined the average single bond strength B_{M-O} of the glasses by means of Equation (7). The obtained data are presented in Table 2, column 3. It is seen that with increasing ZnO and decreasing BaO content the single bond strength show small increase from 251.2 to 253.7 kJ/mol. These values of B_{M-O} suggest predominantly ionic character of the bonds in the glass structure. Probably V-NBO, V-O-Zn along with V-O-V chemical bonds are formed in their structure. Similar type of bonds namely Te-NBO, Te-O-Te, Bi-O-M (M=B, P, Si and Ge) and Bi-O-Bi with high ionic contribution are formed in the structure of tellurite and bismuthate glasses [24, 25].

Table 2. Composition, refractive index n_0, single bond strength B_{M-O}, interaction parameter A and third-order nonlinear optical susceptibility $\chi^{(3)}$ of ZnO-BaO-V_2O_5 glasses.

Composition	n_0	B_{M-O}, kJ/mol	A, Å^{-3}	$\chi^{(3)}$ (n_0). 10^{-12}, esu
1ZnO.34BaO.65V_2O_5	2.421	251.2	0.049	2.24
3ZnO.32BaO.65V_2O_5	2.406	251.5	0.050	2.11
5ZnO.30BaO.65V_2O_5	2.372	251.8	0.050	1.84
7ZnO.28BaO.65V_2O_5	2.227	252.0	0.050	0.99
10ZnO.25BaO.65V_2O_5	2.147	252.4	0.051	0.68
15ZnO.20BaO.65V_2O_5	2.133	253.1	0.052	0.64
20ZnO.15BaO.65V_2O_5	2.112	253.7	0.053	0.58

Interaction parameter of the glasses

Yamashita and Kurosawa [27] 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. 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. Dimitrov and Komatsu have proposed approach for calculation of the interaction parameter in the case of oxide glasses [8,26]. According to this approach the interaction parameter of ZnO-BaO-V_2O_5 glasses was calculated by us using the following equation, where X_{ZnO}, X_{BaO} and X_{V2O5} are equivalent fractions based on the amount of oxygen each oxide contributes to the overall glass stoichiometry, α_{O2-} is oxide ion polarizability in the glass and α_{Zn}^{2+}, α_{Ba}^{2+}, and α_{V}^{5+} are cation polarizabilities. Pauling's value of 3.921 Å^3 for the electronic polarizability of the free oxide ion is used. The calculated data of interaction parameter of ternary ZnO-BaO-V_2O_5 glasses are given in Table 2, column 4. The glasses possess small values of the interaction parameter in

$$A = X_{ZnO}\frac{(3{,}921-\alpha_{O^{2-}})}{2(\alpha_{Zn^{2+}}+3{,}921)(\alpha_{O^{2-}}+\alpha_{Zn^{2+}})} + X_{BaO}\frac{(3{,}921-\alpha_{O^{2-}})}{2(\alpha_{Ba^{2+}}+3{,}921)(\alpha_{O^{2-}}+\alpha_{Ba^{2+}})} + X_{V_2O_5}\frac{(3{,}921-\alpha_{O^{2-}})}{2(\alpha_{V^{5+}}+3{,}921)(\alpha_{O^{2-}}+\alpha_{V^{5+}})} \quad (8)$$

the 0.049-0.053 $Å^{-3}$ range. Small interaction parameter means week interionic interactions resulting in large unshared electron density at one averaged oxide ion. Since both interaction parameter $A(n_0)$ and average single bond strength B_{M-O} are assigned to an average chemical bond M-O in the glass structure, it is of scientific interest to investigate the correlation between them. For that purpose we have plotted the data of interaction parameter A against the data of single bond strength B_{M-O} of ZnO-BaO-V_2O_5 glasses in Fig. 3. A systematic increase in the interaction parameter with composition corresponds to a systematic increase in the average single bond strength. Simultaneously, the average single bond strength and interaction parameter of the ternary vanadate glasses are close to these of pure V_2O_5 (B_{V-O}=313 kJ/mol and $A(n_o)$=0.057 $Å^{-3}$) which means that the interaction along V-O bonds in ternary glasses have significant effect [26].

IR spectra of ZnO-BaO-V_2O_5 glasses

The IR-spectra of ZnO-BaO-V_2O_5 are presented in Fig 4. Three well defined maxima at 910 cm^{-1}, 796-774 cm^{-1} and 658 cm^{-1} are outlined in the IR spectra of the glasses with small ZnO (1-5 mol%). A

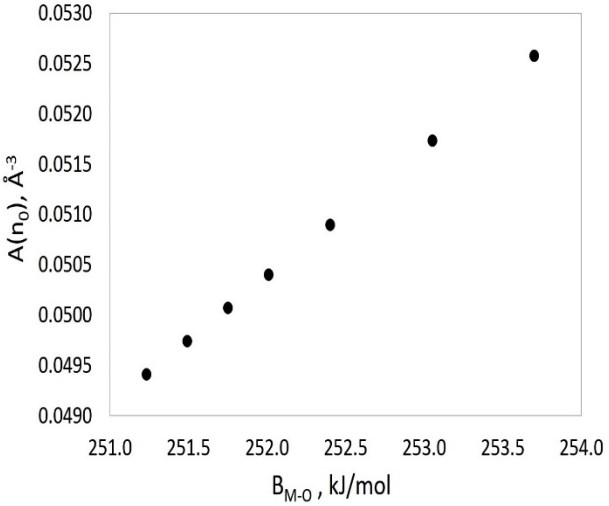

Fig. 3. Interaction parameter as a function of single bond strength of the glasses.

shoulder appears at 972-969 cm^{-1} and the band at 796-774 cm^{-1} disappears in the spectra of glasses containing 7-20 mol% ZnO. At the same time, the intensity of the band at 910 cm^{-1} decreases and the band is shifted to lower frequencies up to 896 cm^{-1}. The assignment of these bonds could be made on the basis of large number of previous results on IR spectra of crystalline and vitreous phases [28-33]. On this basis the band at 910 cm^{-1} is assigned to symmetrical stretching vibrations $\nu^{s}_{VO_2}$ of free VO_2 groups of the VO_4 tetrahedra from $(VO_3)_n$ chains

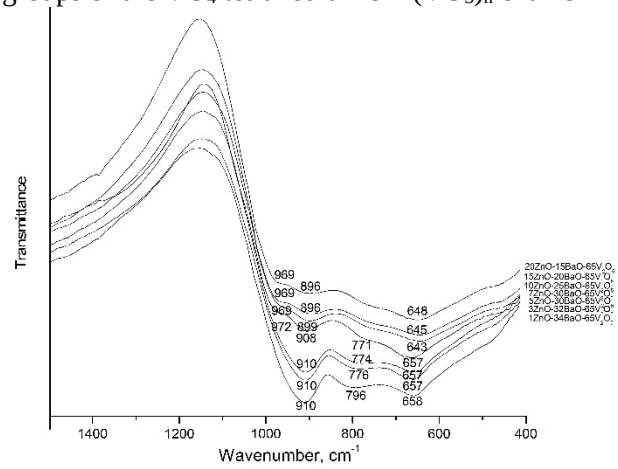

Fig. 4. IR spectra of ZnO-BaO-V_2O_5 glasses.

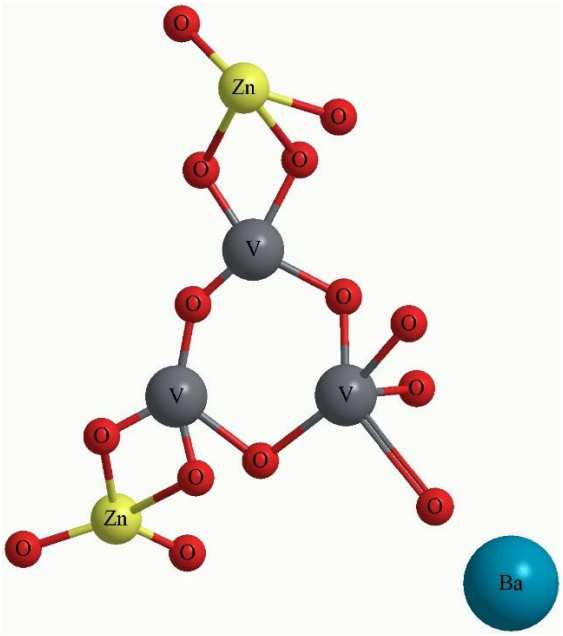

Fig. 5. Structural model for glass with high ZnO content.

while the band at 796-774 cm^{-1} could be attributed to asymmetrical stretching vibrations $\nu^{as}_{VO_2}$ of these groups. The appearance of the shoulder at 972-969 cm^{-1} could be connected with the transformation of part of VO_4 tetrahedra into VO_5 trigonal bipyramids. VO_5 groups are formed in the structure of crystalline and vitreous V_2O_5. Their IR spectra show band at 1020 cm^{-1}, assigned to the vibrations of isolated V=O bonds in VO_5 trigonal bipyramids [28]. According to the mechanism suggested in Ref. 28 Ba^{2+} ions occupy a position between V-O-V layers. This is why they have a direct influence on the isolated V=O bonds of the VO_5 groups according to the scheme:

$$Ba^{2+}\cdots O=V^{5+}$$

This leads to an elongation of the affected V=O bonds and a drop in the frequency down to 972-969

cm^{-1}. The shift of the band at 910 cm^{-1} to lower frequencies up to 896 cm^{-1} could be explained with formation of V-O-Zn bridging bonds created by the influence of Zn^{2+} ion on non-bridging oxygen from VO_2 groups. According to Ref. 33 the band at 658-648 cm^{-1} could be assigned to asymmetrical stretching vibrations ν_{V-O-V}^{as}. At the same time the shift to lower frequencies with increase of ZnO content is probably due to Zn-O vibrations of tetrahedral ZnO_4. Such vibrations in the spectra of glasses were reported in the range of 550-400 cm^{-1} [34]. On the basis of obtained IR spectral results we presented in Fig 5 possible structural model of glass with high ZnO content. VO_4, VO_5 and ZnO_4 groups participating in the model. V-O-V, V-O-Zn and $Ba^{2+\cdots}O=V^{5+}$ chemical bonds are formed between the groups.

Third order nonlinear optical susceptibility of the glasses

The third order nonlinear susceptibility $\chi^{(3)}$ of $ZnO\text{-}BaO\text{-}V_2O_5$ glasses was estimated by generalized Miller's rule,

$$\chi^{(3)} = \left[\chi^{(1)}\right]^4 . 10^{-10}, esu \qquad (9)$$

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

$$\chi^{(1)} = \frac{n_0^2 - 1}{4\pi} \qquad (10)$$

The obtained data are presented in Table 2, column 5. $ZnO\text{-}BaO\text{-}V_2O_5$ glasses show high values of the third order nonlinear optical susceptibility in the 0.58-2.24 x 10^{-12} esu range, which is about 100 times larger than that of pure silica glass ($2.8x10^{-14}$ esu). The obtained results are in good agreement with the experimental data obtained by Hashimoto and Yoko [12] for the third order nonlinear optical susceptibility of thin films of V_2O_5 ($\chi^{(3)}$=$1.1x10^{-11}$ esu). This means that $ZnO\text{-}BaO\text{-}V_2O_5$ glasses are probably good candidates for nonlinear optical applications. Recently, detailed analysis was made on the relationship between electronic oxide ion polarizability and third nonlinear optical susceptibility of different binary oxide glasses [35]. It was established that third nonlinear optical susceptibility $\chi^{(3)}$ of the glasses increases with increasing electronic oxide ion polarizability, that is optical basicity. This is associated with the high electron donor ability of the oxide ion and the high refractive index. In this connection we have plotted the data of the third order nonlinear optical susceptibility $\chi^{(3)}$ as a function of refractive index n_o of $ZnO\text{-}BaO\text{-}V_2O_5$ glasses in Fig. 6. It is seen that $\chi^{(3)}$ increases with increasing the refractive index. The high values of the third order nonlinear optical susceptibility of $ZnO\text{-}BaO\text{-}V_2O_5$ could be attributed to the presence of V-O-Zn, V-O-V and $Ba^{2+\cdots}O=V^{5+}$ bonds in their glass structure. Such bonds were confirmed by the IR spectra. Probably, the high electronic polarizability of the oxide ions in these bonds is responsible for high optical nonlinearity of the glasses.

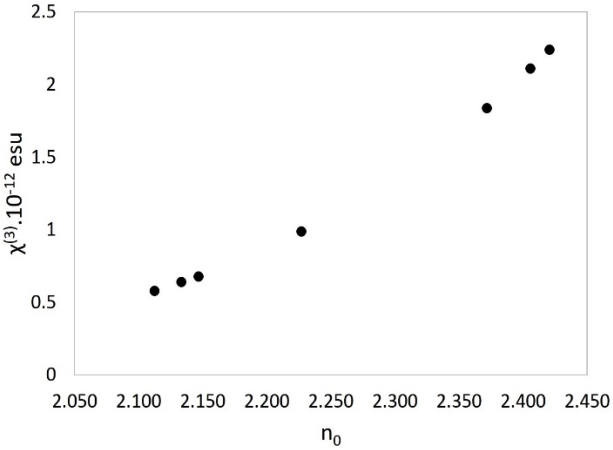

Fig. 6. Third order nonlinear optical susceptibility as a function of refractive index of the glasses.

CONCLUSIONS

Ternary $ZnO\text{-}BaO\text{-}V_2O_5$ glasses have been investigated by means of XRD, DTA and DSC analysis. XRD analysis confirmed amorphous nature of the samples. DTA and DSC analysis show that the glasses possess low glass transition temperatures T_g of 262^o – 303 ℃ and crystallization temperatures T_x 315^o – 372℃. The experimental density was found to be in 3.974-3.245 g/cm^3 range. The polarizability approach based on Lorentz-Lorenz equation has been applied to $ZnO\text{-}BaO\text{-}V_2O_5$ glasses. With a view to elucidate theoretical refractive index, electronic ion oxide polarizability and optical basicity of the glasses was calculated. It was established that the glasses possess high refractive index (2.421-2.112), high electronic ion polarizability (2.725 - 2.692 Å^3) and high optical basicity (1.050-1.057). 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 0.58-2.24 $x10^{-12}$ 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 V-O-Zn, V-O-V and $Ba^{2+\cdots}O=V^{5+}$ where 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. Structural model of glass with high ZnO content containing VO_4, VO_5 and ZnO_4 groups is proposed.

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ЕЛЕКТРОННА ПОЛЯРИЗУЕМОСТ, ОПТИЧЕСКА ОСНОВНОСТ И ХИМИЧЕСКО СВЪРЗВАНЕ НА ЦИНК-БАРИЙ-ВАНАДАТНИ ОКСИДНИ СТЪКЛА

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(Резюме)

Стъкла със състави xZnO.(35-x)BaO.65V_2O_5 (x= 1, 3, 5, 7, 10, 15 и 20 мол %) бяха синтезирани посредством рязко охлаждане на стопилки. Пробите бяха анализирани посредством рентгеноструктурен и термичен анализ. Резултатите от рентгеноструктурния анализ доказаха аморфната природа на образците. Трикомпонентните стъкла притежават ниски температури на застъкляване T_g и кристализация T_x. Измерената плътност намалява с увеличаване съдържанието на ZnO от 3.974 g/cm^3 до 3.245 g/cm^3. Теоретичния показател на пречупване на светлината, кислородната електронна поляризуемост и оптическата основност на стъклата беше изчислена посредством уравнението на Лорентц-Лоренц. Стъклата притежават висок показател на пречупване (2.112-2.421), висока кислородна електронна поляризуемост (2.692-2.725 $Å^3$) и висока оптическа основност (1.050-1.057). Нелинейната оптическа възприемчивост от трети порядък $\chi^{(3)}$ беше определена посредством Милеровото правило. Беше установено, че стъклата притежават високи стойности за $\chi^{(3)}$ (0.58-2.24x10^{-12} esu). Средната здравина на химичната връзка B_{M-O} и параметъра на междуйонно взаимодействие A(n_o) също бяха изчислени. Здравината на химичната връзка варира в граници от 251 до 253 kJ/mol , а параметъра на междуйонно взаимодействие от 0.049 до 0.053 $Å^{-3}$, което предполага наличието на слаби химични връзки. Такива връзки, а именно Ba…O=V, V-NBO (немостови кислород), V-O-Zn и V-O-V бяха потвърдени с инфрачервена спектроскопия. Високата поляризуемост на кислородните йони в тези връзки е причината за наблюдаваните линейни и нелинейни оптични свойства на стъклата. Предложен е структурен модел на стъкла съдържащи VO_5, VO_4 и ZnO_4 групи.