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SYNTHESIS, OPTICAL PROPERTIES AND STRUCTURE OF NiO-BaO-V_2O_5 GLASSES

Tina Tasheva, Vesselin Dimitrov

Department of Silicate Technology
University of Chemical Technology and Metallurgy
8 Kl. Ohridski, Sofia 1756, Bulgaria
E-mail: vesselin@uctm.edu

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ABSTRACT

Glasses with compositions xNiO.(35-x)BaO.65V_2O_5 (x= 1, 3, 5, 7, 10, 15 and 20 mol %) are prepared using a conventional melt quenching method. XRD and DTA/DSC analysis are performed. The results of XRD analysis confirm the amorphous nature of the samples. The glasses possess low glass transition temperature T_g of 267 - 282 A and crystallization temperature of 301 - 390°C The measured density decreases with increasing of NiO content from 3.560 to 3.490 g cm^{-3}. The refractive index n_0, optical band gap E_g, electronic oxide ion polarizability $\alpha_{O^{2-}}$ and optical basicity Λ of the glasses are calculated by Lorentz-Lorenz equation. The glasses were found to possess high refractive index (2.174 - 2.271), narrow band gap (3.51 - 3.98 eV), high oxide ion polarizability (2.653 - 2.723 $Å^3$) and high optical basicity (1.041 - 1.057). The third order nonlinear optical susceptibility $\chi^{(3)}$ is determined by generalized Miller's rule and three photon model. It was established that $\chi^{(3)}$ is high in the 0.78 - 1,43x10^{-12} esu range. The average single bond strength B_{M-O} and the interaction parameter $A(n_0)$ are calculated. The bond strength is found to vary from 252 - 258 kJ mol^{-1} and the interaction parameter was in the 0.050 - 0.055 $Å^{-3}$ range, thus suggesting the presence of weak chemical bonds. The structure of the glasses was investigated by means of IR spectroscopy. The analysis of IR spectra confirmed the presence of weak chemical bonds such as Ni-O-V, Ba…O=V, V-NBO (nonbridging oxygen) and V-O-V. The high polarizability of the oxide ions in these bonds accounts for the observed linear and nonlinear optical properties of the glasses.

Keywords: oxide glasses, polarizability, IR-spectra, chemical bonding, optical nonlinearity.

INTRODUCTION

V_2O_5 based crystals, glasses, thin films and nanostructured materials play an important role in the fields of materials science since they have potential applications as semi-conducting materials, power cells, electrochromic materials, battery electrodes, catalysts, gas sensors, thermochromic materials, thin film batteries, IR detectors, etc. [1 - 5]. Among large number of V_2O_5 based materials the vanadate glasses have attracted much attention especially due to their interesting electrical and optical properties. It is well-known that they belong to the class of amorphous semiconductors possessing electronic conductivity [6, 7]. Such glasses are good candidates for electronical memory switching devices [8]. On the other hand, vanadate glasses possess high potential for application in the field of laser related fiber optics and nonlinear optics. Peng et al. [9] have reported data about neodymium-doped vanadate glass with remarkable optical transmission suitable for optical applications. Recently, 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 [10, 11]. 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 [12 - 14]. The obtained values of $\chi^{(3)}$ based on experimental data and generalized Miller's rule are rather large, indicating that such glasses are interesting materials for non-linear optical devices.

NiO is an attractive material due to its useful optical, electrical, magnetic, electronic and catalytic properties

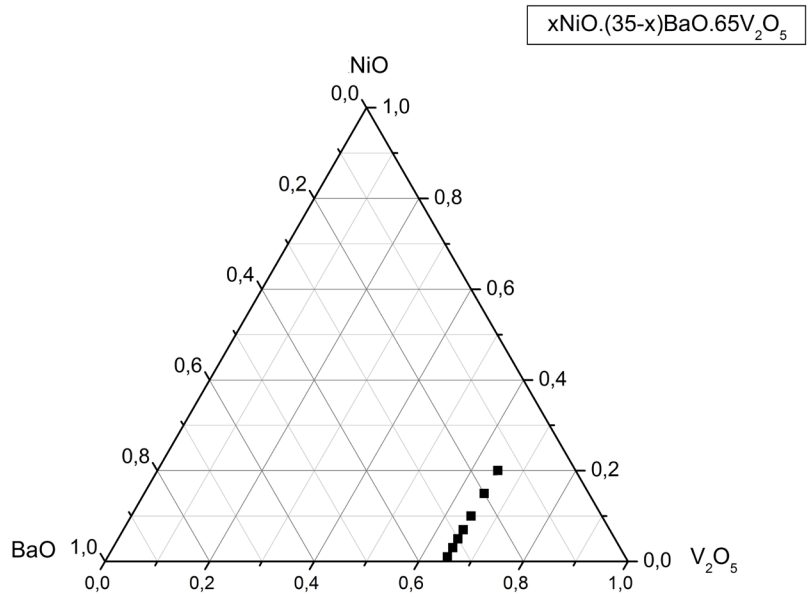

Fig. 1. Glass compositions in NiO-BaO-V_2O_5 ternary system.

[15, 16]. NiO is a promising material for many applications such as a positive electrode in batteries, solar thermal absorber, catalysts and electrochromic devices [17-19]. Pure stoichiometric NiO crystals are perfect insulators [17]. NiO has interesting properties as nanomaterial too. Nickel oxide nanoparticles are used as cathode materials for alkaline batteries, electrochromical supercapacitators, smart windows, active layers for gas sensors, dye-sensitized photocathodes, recording materials, ceramic materials, etc . [20, 21]. Non-stoichiometric NiO is a good P-type semiconductor and potential gas sensor [21]. Recently, nonlinear optical properties of NiO have been investigated. De Melo et al. [22] have performed Z-scan nonlinear measurements and they have obtained large value of nonlinear refractive index $n_2 \approx 10^{-12}$ cm^2/W of NiO thin film. Al-Ghamdi et al. [23] have estimated third order nonlinear optical susceptibility $\chi^{(3)}$ of NiO thin film in the order of 1.62×10^{-13} esu.

On the basis of the mentioned above it is of scientific and practical interest to check the joint influence of V_2O_5 and NiO 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 NiO-BaO-V_2O_5 glasses and have looked for some intrinsic relationship between them and predicted third order nonlinear optical susceptibility. The structure of the glasses and the correlation between the structure and the investigated parameters have been also discussed.

Table 1. Composition, molar mass M, density d, molar volume V_m, electronic oxide ion polarizability $\alpha_{O^{2-}}$ optical basicity Λ and molar refraction R_m of NiO-BaO-V_2O_5 glasses.

Composition	M, g mol^{-1}	d, g cm^{-3}	V_m, cm^3 mol^{-1}	$\alpha_{O^{2-}}$, Å^3	Λ	R_m, cm^3 mol^{-1}
1NiO.34BaO.65V_2O_5	171.10	3.560	48.06	2.723	1.057	26.63
3NiO.32BaO.65V_2O_5	169.53	3.551	47.74	2.715	1.055	26.56
5NiO.30BaO.65V_2O_5	167.96	3.546	47.37	2.708	1.053	26.50
7NiO.28BaO.65V_2O_5	166.39	3.538	47.03	2.700	1.052	26.43
10NiO.25BaO.65V_2O_5	164.03	3.527	46.51	2.689	1.049	26.33
15NiO.20BaO.65V_2O_5	160.09	3.498	45.77	2.671	1.045	26.16
20NiO.15BaO.65V_2O_5	156.16	3.490	44.75	2.653	1.041	25.99

EXPERIMENTAL

Glasses with composition of xNiO.(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. The glass compositions are given in Fig. 1 and Table 1, column 1. Chemical powders of reagent grade NiO, 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. The densities of the glasses at room temperature were determined by pycnometer using distilled water as immersion liquid. The amorphous nature of the samples was identified using X-Ray diffractometer Philips APD15 Cu k_α graphite monochromator. 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}. DTA and 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.

RESULTS AND DISCUSSION

Density, X-ray diffraction and DTA/DSC analysis of the glasses

The obtained results of the density of the glass samples are in the 3.560 - 3.490 g cm^{-3} range and are presented in Table 1, column 3. The density as a function of the composition is shown in Fig. 2. It can be seen that with increasing NiO content the density decreases.

An example of X-ray diffraction pattern of 5NiO.30 BaO.$65V_2O_5$ glass is presented in Fig. 3. The result shows no sharp peak which indicates the absence of crystalline nature. The curve shows only broad diffuse scattering at about 26 and 42 2Θ angles which is characteristic of near range order. This ensures the amorphous nature of the investigated glasses.

The glasses possess low glass transition temperatures T_g of 282 - 267℃ and crystallization temperatures T_x of 390 - 301℃. For example the DSC curve of glass with composition 15NiO.20BaO.$65V_2O_5$ is shown in Fig. 4.

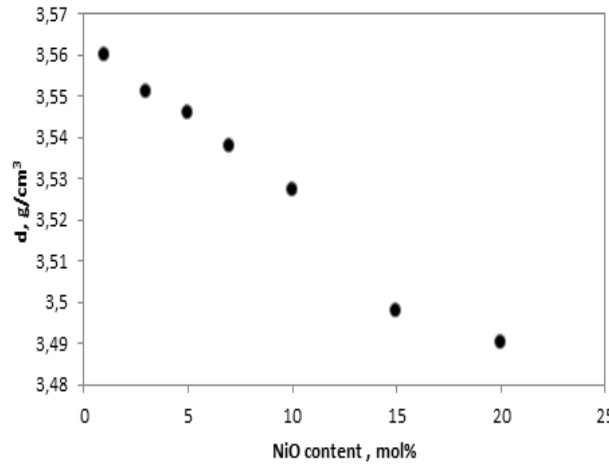

Fig. 2. Density as a function of NiO content.

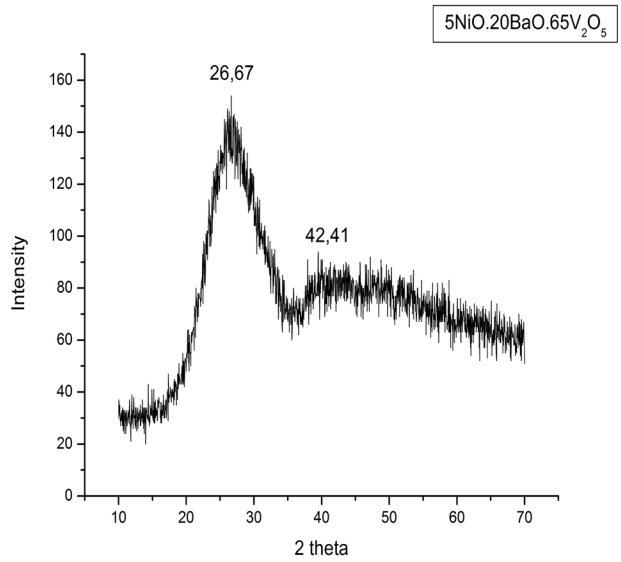

Fig. 3. XRD pattern of glass with composition 5NiO.30BaO. $65V_2O_5$.

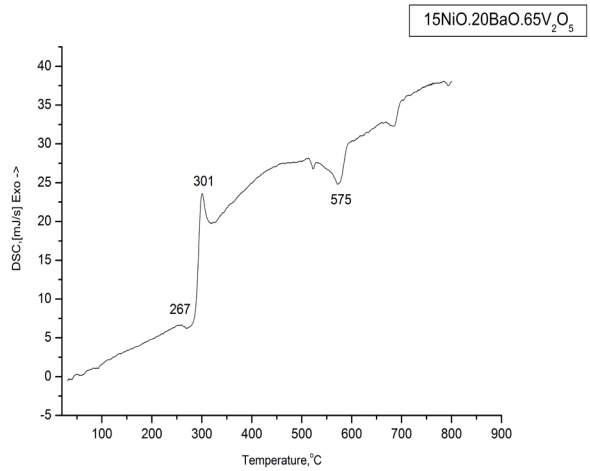

Fig. 4. DSC curve of glass with composition 15NiO.30BaO. $65V_2O_5$.

Optical properties of NiO-BaO-V_2O_5 glasses

Electronic polarizability and optical basicity of the glasses

The Lorentz-Lorenz equation underlies of so called polarizability approach and relates molar refraction R_m to refractive index n_o and molar volume V_m of the substance by,

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

This equation gives the average molar refraction of isotropic substances, i.e., for liquids, glasses and cubic crystals. When Avogadro's number N_A is introduced, the molar refraction R_m can be expressed as a function of molar polarizability a_m,

$$\boldsymbol{R_m} = \frac{4\pi\alpha_{\boldsymbol{m}}\boldsymbol{N_A}}{3} \quad (2)$$

with a_m in (Å^3) this equation can be transformed to,

$$R_m = 2.52 a_m \quad (3)$$

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

$$R_m = 2.52(\sum a_i + N a_{O^{2-}}) = \\ = 2.52(\mathrm{a}.\alpha_{Ni^{2+}} + b.a_{Ba^{2+}} + c.\alpha_{V^{5+}} + N.\alpha_{O^{2-}}) \quad (4)$$

where $\sum a_i$ denotes molar cation polarizability, $\alpha_{Ni^{2+}}$ $a_{Ba^{2+}}$ and $\alpha_{V^{5+}}$ are cation polarizabilities of Ni^{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 [24] the cation polarizabilities are: $\alpha_{Ni^{2+}}$ = 0,266 Å^3; $a_{Ba^{2+}}$ = 1,595 Å^3; $\alpha_{V^{5+}}$ = 0,122 Å^3.

The electronic oxide ion polarizability $\alpha_{O^{2-}}$ which participate in Eq. 4 we have calculated from theoretical optical basicity Λ_{th} of NiO-BaO-V_2O_5 glasses in accordance with the approach proposed by Duffy and Ingram [25]:

$$\Lambda_{th} = X_{NiO}\Lambda_{NiO} + X_{BaO}\Lambda_{BaO} + X_{V_2O_5}\Lambda_{V_2O_5} \quad (5)$$

where X_{NiO}, 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_{NiO}, Λ_{BaO} and $\Lambda_{V_2O_5}$ are optical basicities of individual oxides (Λ_{NiO} = 0,915; Λ_{BaO} = 1,22 and $\Lambda_{V_2O_5}$ = 1,04 [26, 27]).

An alternative approach for determination of optical basicity seems to be the relationship between basicity and refractivity. Duffy [28] has established that an intrinsic relationship exists between electronic polarizability of the oxide ions $\alpha_{O^{2-}}$ and optical basicity of the oxide medium Λ, as given by Eq. (6):

$$\Lambda = 1,67\left(1 - \frac{1}{\alpha_{O^{2-}}}\right) \quad (6)$$

Based on Eq. (6) the oxide ion polarizability can be calculated by using this equation:

$$\alpha_{O^{2-}} = \frac{1,67}{1,67 - \Lambda} \quad (7)$$

The oxide ion polarizability $\alpha_{O^{2-}}$ of NiO-BaO-V_2O_5 glasses was determined my means of Eq. (7). On the basis of the data for oxide ion polarizability the molar refraction R_m of the glasses was calculated using Eq. (4) taking into account also the cation polarizabilities of Ba^{2+}, Ni^{2+} and V^{5+} mentioned above. The molar volume V_m was estimated on the basis of the molar mass and the density of the glasses. The data for molar volume V_m, oxide ion polarizability $\alpha_{O^{2-}}$, theoretical optical basicity Λ_{th} 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 (2.723 - 2.653 Å^3) which indicate for their basic nature.

Refractive index and optical band gap of the glasses

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

$$n_0 = \sqrt{\frac{V_m + 2R_m}{V_m - R_m}} \quad (8)$$

We have estimated the theoretical refractive index n_o of NiO-BaO-V_2O_5 glasses using Eq. 8. The data are listed in Table 2, column 2. As can be seen the glasses possess high values of refractive index in the 2.174 - 2.271 range. The results shown in Table 2 are in good agreement with experimental data for refractive indices of thin films of V_2O_5 (n_o = 2.59) and crystalline NiO (n_o = 2,1818) [10, 24].

On the other hand, Duffy [29] has obtained an

Table 2. Compositions, refractive index n_0, optical band gap E_g and third order nonlinear optical susceptibility $\chi^{(3)}$ obtained by Miller's rule and Three-photon model.

Composition	n_0	E_g, eV	Miller's rule	Three photon model
			$\chi^{(3)}.10^{-12}$, esu	$\chi^{(3)}.10^{-12}$, esu
1NiO.34BaO.65V_2O_5	2.174	3.977	0.78	0.78
3NiO.32BaO.65V_2O_5	2.182	3.936	0.81	0.82
5NiO.30BaO.65V_2O_5	2.193	3.883	0.85	0.88
7NiO.28BaO.65V_2O_5	2.202	3.837	0.88	0.93
10NiO.25BaO.65V_2O_5	2.217	3.765	0.94	1.01
15NiO.20BaO.65V_2O_5	2.237	3.670	1.03	1.15
20NiO.15BaO.65V_2O_5	2.271	3.512	1.20	1.43

empirical formula that relates energy gap E_g to molar refraction R_m for a large number of simple oxides,

$$E_g = 20.\left(1-\frac{R_m}{V_m}\right)^2 \quad (9)$$

We have used Eq. (9) to calculate the energy gap of NiO-BaO-V_2O_5 glasses. The obtained data are presented in Table 2, column 3. As can be seen the glasses have narrow energy gap. The increasing of NiO content leads to decreasing of the energy gap from 3.98 eV to 3.51 eV. The results shown in Table 2 are in agreement with experimental data for energy gap of crystalline NiO (E_g = 3.80 eV) [24].

Third order nonlinear optical susceptibility of the glasses

The third order nonlinear optical susceptibility $\chi^{(3)}$ in esu of NiO-BaO-V_2O_5 glasses was estimated by generalized Miller's rule [30],

$$\chi^{(3)} = \left[\chi^{(1)}\right]^4 .10^{-10} \quad (10)$$

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

$$\chi^{(1)} = \frac{n_0^{\,2}-1}{4\pi} \quad (11)$$

and three photon model [10]

$$\chi^{(3)} = \frac{\Phi}{\left(E_g - 1{,}96\right)\left(E_g - 1{,}31\right)\left(E_g - 0{,}65\right)} \quad (12)$$

where Φ is a constant equal to $1{,}4.10^{-11}$; E_g - optical band gap.

The obtained data are presented in Table 2, columns 4 and 5. NiO-BaO-V_2O_5 glasses show high values of the third order nonlinear optical susceptibility in the 0,78 - $1{,}43x10^{-12}$ esu range. It is seen that good agreement exists between the data obtained on the basis of different initial quantities namely refractive index n_0 and energy gap E_g. Obviously both parameters are very important for the origin of the third order nonlinear optical susceptibility $\chi^{(3)}$. The obtained results are in good agreement with the experimental obtained data by Hashimoto et al. [10] for the third order nonlinear optical susceptibility of thin films of V_2O_5 ($\chi^{(3)} = 1.1x10^{-11}$ esu) and these reported by Al-Ghamdi [23] for thin film of NiO ($\chi^{(3)} = 1.62x10^{-13}$ esu). This means that NiO-BaO-V_2O_5 glasses are probably good candidates for nonlinear optical applications. We have plotted the data of the third order nonlinear optical susceptibility $\chi^{(3)}$ as a function of refractive index n_o and energy gap E_g of NiO-BaO-V_2O_5 glasses in Figs. 5 and 6. It is seen that $\chi^{(3)}$ increases with increasing the refractive index and decreasing the energy gap. The high values of the third order nonlinear optical susceptibility of NiO-BaO-V_2O_5 could be probably attributed to the presence of weak chemical bonds with increased ionicity in their glass structure.

Structure of NiO-BaO-V_2O_5 glasses

Average single bond strength of the glasses

Based on Sun's fundamental condition of glass formation [31] Dimitrov and Komatsu [32] 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 NiO-BaO-V_2O_5 glasses

the following equation can be used:

$$B_{M-O} = xB_{Ni-O} + yB_{Ba-O} + (1-x-y)\,B_{V-O} \quad (13)$$

where $B_{Ni-O,}$ B_{Ba-O} and B_{V-O} are single bond strength of M-O in the corresponding individual oxide. It has been clarified from UV-VIS-NIR, EXAFS and XANES spectra of silicate and phosphate glasses that coordination number of Ni^{2+} cation varies from 4 to 6 and NiO_4, NiO_5 and/or NiO_6 groups can be formed in the structure depending on the glass composition [33 - 35]. Mostly NiO_4 groups are found in the structure of $K_2NiSi_3O_8$ (K_2O. $NiO.3SiO_2$) and $Na_2NiSi_3O_8$ ($Na_2O.NiO.3SiO_2$) glasses. The molar ration of our compositions with high NiO content is close to that of the glasses mentioned above. That is why we calculated the single bond strength of NiO-BaO-V_2O_5 glasses using coordination number of Ni^{2+} CN = 4. According to Sun and Huggins [36] the dissociation energy of NiO is 166 kcal mol^{-1}. Therefore,

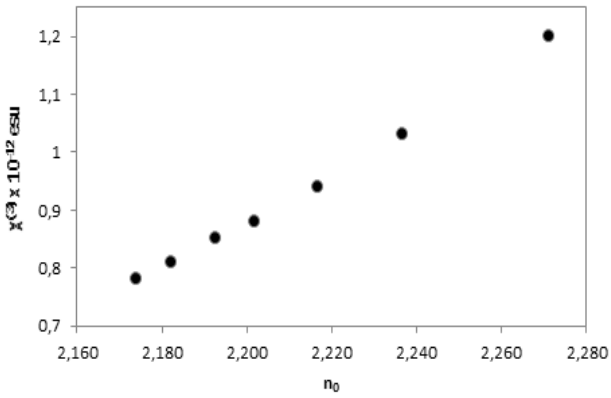

Fig. 5. Third order nonlinear optical susceptibility as a function of refractive index of the glasses.

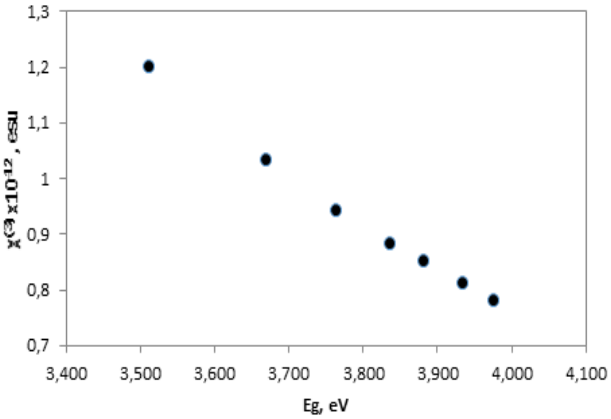

Fig. 6. Third order nonlinear optical susceptibility as a function of optical band gap of the glasses.

the single bond strength of Ni-O in NiO_4 group is 41,7 kcal mol^{-1} or 174 kJ mol^{-1}. We have determined the average single bond strength B_{M-O} of the glasses by means of Eq. (13) using values of 138 kJ mol^{-1} for BaO and 313 kJ mol^{-1} for V_2O_5 (see Ref. 37) and 174 kJ mol^{-1} for NiO determined in the present paper. The obtained data are presented in Table 3, column 2. It is seen that with increasing NiO and decreasing BaO content the single bond strength increases from 251 to 285 kJ mol^{-1}. The values of the single bond strength of NiO-BaO-V_2O_5 glasses are close to those of tellurite, bismuthate and other vanadate glasses [12-14, 32, 37]. Probably, weak chemical bonds such as V-NBO, V-O-Ni along with V-O-V are formed in their structure.

Interaction parameter of the glasses

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 [38] the interaction parameter A of NiO-BaO-V_2O_5 glasses was calculated by us using the following equation,

$$A = X_{NiO}\frac{(3,921-\alpha_{O^{2-}})}{2(\alpha_{Ni^{2+}}+3,921)(\alpha_{O^{2-}}+\alpha_{Ni^{2+}})} + X_{BaO}\frac{(3,921-\alpha_{O^{2-}})}{2(\alpha_{Ba^{2+}}+3,921)(\alpha_{O^{2-}}+\alpha_{Ba^{2+}})} + X_{V_2O_5}\frac{(3,921-\alpha_{O^{2-}})}{2(\alpha_{V^{5+}}+3,921)(\alpha_{O^{2-}}+\alpha_{V^{5+}})} \quad (14)$$

where X_{NiO}, X_{BaO} and X_{V2O5} are equivalent fractions based

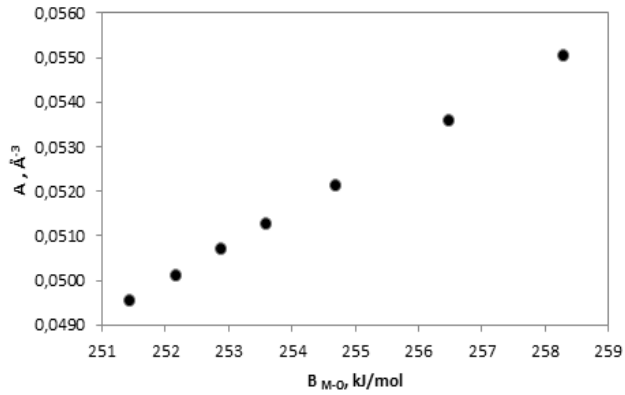

Fig. 7. Interaction parameter as a function of single bond strength of the glasses.

Table 3. Composition, single bond strength B_{M-O}, interaction parameter A and metallization criterion $M(n_0)$ of NiO-BaO-V_2O_5 glasses.

Composition	B_{M-O}, kJ mol^{-1}	A, Å^{-3}	$M(n_0)$
1NiO.34BaO.65V_2O_5	251.5	0.0495	0.446
3NiO.32BaO.65V_2O_5	252.2	0.0501	0.444
5NiO.30BaO.65V_2O_5	252.9	0.0507	0.441
7NiO.28BaO.65V_2O_5	253.6	0.0512	0.438
10NiO.25BaO.65V_2O_5	254.7	0.0521	0.434
15NiO.20BaO.65V_2O_5	256.5	0.0536	0.428
20NiO.15BaO.65V_2O_5	258.3	0.0550	0.419

on the amount of oxygen each oxide contributes to the overall glass stoichiometry, $\alpha_{O^{2-}}$ is oxide ion polarizability of the glass and $\alpha_{Ni^{2+}}$, $\alpha_{Ba^{2+}}$, and $\alpha_{V^{5+}}$ 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 NiO-BaO-V_2O_5 glasses are given in Table 3, column 3. The glasses possess small values of the interaction parameter in the 0.050 - 0.055 Å^{-3} range. The interaction parameter is a quantitative measure for the interionic interaction of negative ions such as O^{2-} with the nearest neighbors (cations). 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 NiO-BaO-V_2O_5 glasses in Fig. 7. As it is seen, a good agreement could be observed between the data based on different initial quantities. A systematic increase in the interaction parameter with composition corresponds to a systematic increase in the average single bond strength.

Metallization criterion

The ratio R_m/V_m is so-called polarizability per unit volume. It can be determined directly from Lorentz-Lorenz equation,

$$\frac{R_m}{V_m} = \frac{n_0^2 - 1}{n_0^2 + 2} \tag{15}$$

According to the Herzfeld theory of metallization the following simple criterion appears to be a necessary and sufficient condition for predicting metallic or insulating behavior in the condensed state [39]:

$R_m/V_m > 1$ (metal) and $R_m/V_m < 1$ (insulator)

On this basis an estimation of the nonmetal/metal behavior of the material is possible. The difference

$$M(n_0) = 1 - \frac{R_m}{V_m} \tag{16}$$

is so-called metallization criterion [30].

Materials with large $M(n_0)$ close to 1 are typical insulators. In opposite small value of $M(n_0)$ close to zero means that the width of both valence and conduction bands become large, resulting in a narrow band gap and increased the metallicity of the solid. It has been established that tellurite glasses containing Nb_2O_5, NiO, WO_3, MoO_3 and lead-titanate glasses possess metallization criterion in the 0.42-0.50 range, while borate, silicate and germanate glasses containing large amount glass-forming oxide have metallization criterion ranging from 0.50 to 0.75 [40]. The small metallization criterion means increased tendency for metallization of the glasses. We calculated the metallization criterion for NiO-BaO-V_2O_5 glasses and data are presented in Table 3, column 4. It is seen that the metallization criterion decreases from 0.446

to 0.419 with increasing NiO content. The obtained values showed that NiO-BaO-V_2O_5 glasses possess increased tendency for metallization of the glasses.

IR-spectra of the glasses

The IR-spectra of NiO-BaO-V_2O_5 glasses are presented in Fig. 8. Three well defined maxima at 904 - 903 cm^{-1}, 656 cm^{-1} and 440 cm^{-1} are outlined in the IR spectra of the glasses with small NiO content (1 - 3 mol %). A shoulder appears at 964 cm^{-1} in the spectra of glasses containing 5 - 10 mol % NiO. The observed shoulder becomes well defined band and new band appears at 827 - 822 cm^{-1} of the spectra of the glasses containing 15 and 20 mol % NiO. At the same time, the intensity of the band at 904 cm^{-1} decreases and the band is shifted to lower frequencies up to 887 cm^{-1}. The band at 444 cm^{-1} also shifts to lower frequencies up to 425 cm^{-1}. The assignment of these bands could be made on the basis of large number of previous results on IR spectra of crystalline and vitreous vanadate phases [41 - 45]. On this basis the band at 904 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. The appearance of the band at 964 - 973 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 [41]. According to the mechanism suggested in Ref. 41 Ba^{2+}, ions occupy a position between V-O-V layers. That 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 964 - 973 cm^{-1}. Simultaneously, the increase of the intensity of the band at 964 - 973 cm^{-1} and decrease of the intensity of the band at 904 - 887 cm^{-1} means that the number of VO_5 groups increases and the number of the VO_4 groups decreases with increasing NiO content. The shift of the band at 904 cm^{-1} to lower frequencies up to 887 cm^{-1} could be explained with formation of V-O-Ni bridging bonds created by the influence of Ni^{2+} ion on non-bridging oxygen from VO_2 groups. Similar band at about 865 cm^{-1} has been observed in the crystalline spectra of ZnV_2O_6 and CdV_2O_6 and it has been assigned to the vibrations of Zn(Cd)-O-V bonds [42]. According

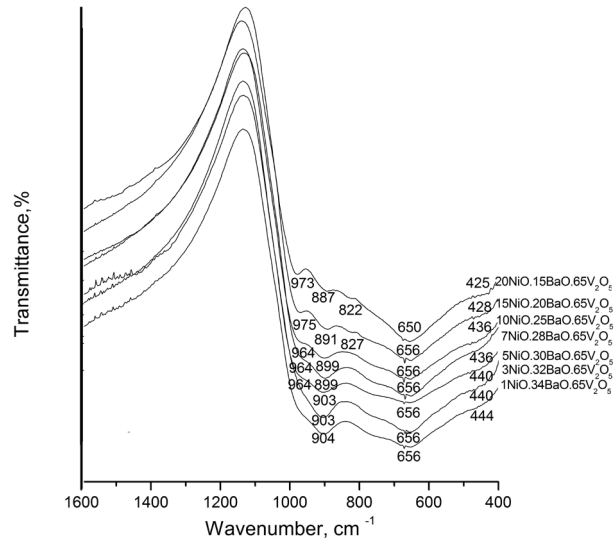

Fig. 8. IR spectra of NiO-BaO-V_2O_5 glasses.

to Ref. 43 the band at 656-650 cm^{-1} could be assigned to asymmetrical stretching vibrations ν^{as}_{V-O-V}. The low frequency band at 444 - 424 cm^{-1} possesses more complicated origin. It is probably a superposition between bending vibration δ_{v-o} of the V-O bonds and the stretching vibrations of Ni-O bonds in NiO_n (n = 4 - 6) groups. It is assumed that mostly NiO_4 groups participate in the structure since as it was mentioned above good correlation exists between interaction parameter A and the single bond strength $B_{M\text{-}O}$ of NiO-BaO-V_2O_5 glasses.

CONCLUSIONS

Ternary NiO-BaO-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 282 - 267°C and crystallization temperatures T_x 390 - 301°C. The experimental density was found to be in 3,56 - 3,49 g cm^{-3} range. The polarizability approach based on Lorentz-Lorenz equation has been applied to NiO-BaO-V_2O_5 glasses. With a view to elucidate theoretical refractive index, electronic oxide ion polarizability, optical basicity and optical band gap of the glasses have been calculated. It was established that the glasses possess high refractive index (2,174 - 2,271), comparatively narrow band gap (3,98 - 3,51 eV), high electronic ion polarizability (2,723 - 2,653 $Å^3$) and high optical basicity (1,041 - 1,057). The theoretical third order nonlinear optical

susceptibility $\chi^{(3)}$ was determined and the glasses possess high values of $\chi^{(3)}$ in the 0,78 - 1,43 x10^{-12} range. It was found that the glasses have small single bond strength and interaction parameter, thus suggesting the presence of weak chemical bonds. Such bonds, namely V-O-Ni, 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.

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