ABSTRACT

Glasses with compositions xB_2O_3.(35-x)BaO.65V_2O_5 (x = 1, 3, 5, 7, 10, 15 mol %) were prepared using a conventional melt quenching method. DTA and DSC analysis were performed. The theoretical refractive index, electronic oxide ion polarizability, optical basicity and optical band gap of the glasses were calculated by Lorentz-Lorenz equation. The glasses were found to possess high refractive index (2.48 - 2.54), narrow band gap (2.54 - 2.71 eV), high oxide ion polarizability (2.41 - 2.70 Å^3) and high optical basicity (1 - 1.05). The third order nonlinear optical susceptibility χ^(3) was determined by generalized Miller’s rule. It was established that χ^(3) is close to the experimental value of 1.1x10⁻¹¹ esu measured for thin film of V_2O_5 by Hashimoto et al. using THG method. The average single bond strength B_M-O and interaction parameter A(n_j) were calculated. The bond strength was found to vary from 255 kJ mol⁻¹ to 305 kJ/mol and interaction parameter was in the 0.05-0.07 Å⁻³ range, thus suggesting the presence of weak chemical bonds. Such bonds, namely Ba...O=V, V-NBO (nonbridging oxygen), V-O-B and V-O-V were confirmed by IR-spectra of the glasses. The high polarizability of the oxide ions in these bonds accounted for the observed linear and nonlinear optical properties of the glasses. A structural model of glasses containing BO_3, B_2O_5, VO_5 and VO_4 groups is proposed.

Keywords: vanadate glasses, refractive index, energy gap, electronic polarizability, optical basicity, chemical bonding, DTA, DSC, IR spectra, nonlinear optical materials.

INTRODUCTION

During the last twenty years large number of third order nonlinear optical materials including crystals, semiconductors, inorganic glasses, chalcogenide glasses, semiconductor and metal doped glasses, inorganic thin films, organic molecules, inorganic-organic composites and conjugated polymers have been studied. Among them the group of non-conventional oxide glasses has attracted much attention due to their unique combination of properties such high linear and nonlinear refractive indices, chemical durability, thermal stability, low melting temperature and ultra fast response time [1]. 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 χ^(3) have been obtained [2, 3]. Also recently, χ^(3) of BaO-V_2O_5 and Fe_2O_3-BaO-V_2O_5 glasses has been predicted [4]. The obtained values of χ^(3) based on the generalized Miller’s rule are rather large, indicating that such glasses are interesting materials for non-linear optical devices. Similar results have been also obtained for high refractive indices lead vanadate amorphous thin films [5].

Since optical nonlinearity is closely related to the electronic polarizability today’s knowledge of the state of polarization of ions in different crystalline and amorphous materials is of significant interest. The estimation of the electronic polarizability of ions is subject of the so-called polarizability approach in glass science [6, 7]. Recently, it has been applied by us for some binary vanadate glasses such as V_2O_5 - P_2O_5, V_2O_5 - GeO_2, SrO - V_2O_5.
and PbO - V2O5 glasses [8]. It has been found that the vanadate glasses possess oxide ion polarizability in the range of ~1.7 - 2.4 Å3 and optical basicity varying from ~0.7 to 1.1.

Almost 65 years ago, Sun [9] has suggested a bond energy criterion for glass formation and has reported comprehensive data on single bond strength BM-O in kcal per Avogadro bond for various simple oxides based on their dissociation energy Ed. Recently, Dimitrov and Komatsu [10] have proposed an approach to the calculation of average single bond strength BM-O of oxide glasses based on Sun’s data of simple oxides. The single bond strength BM-O of V2O5 - P2O5, V2O5 - GeO2, SrO - V2O5 and PbO - V2O5 glasses has been also estimated [8]. It has been established that the optical basicity of glasses increases with the decrease of the single bond strength. It is of scientific and practical interest to search similar data for other binary and multi-component vanadate glasses.

In this connection we have estimated in this study the oxide ion polarizability, the optical basicity, the linear refractive index, the optical band gap, the average single bond strength, the interaction parameter, and the third order nonlinear optical susceptibility of B2O3 - BaO - V2O5 glasses and have looked for some intrinsic relationship between them. The structure of the glasses has been also discussed.

**EXPERIMENTAL**

Glasses with compositions of xB2O3.(35-x)BaO.65V2O5 (x = 1, 3, 5, 7, 10 and 15 mol %) were prepared using a conventional melt-quenching method. Reagent grade commercial powders of BaCO3, H3BO3 and V2O5 were mixed together and melted in a porcelain crucible at 800°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 densities of the glasses were determined at room temperature using data for simple oxides. 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 recorded in air. The scans were performed at 10°C min−1 using STAPEPT 1600 TG-DTA/DSC LINSEIS Messgerate GmbH calorimeter. The glass transition temperature TG and crystallization temperature TX were estimated on the ground of the DSC curves.

**RESULTS AND DISCUSSION**

**Polarizability and basicity of B2O3-BaO-V2O5 glasses**

The most familiar and widely used relationship in the polarizability approach is the Lorentz-Lorenz equation which relates the molar refraction, Rm, to the refractive index, n o, and the molar volume, V m, of the substance by:

\[
R_m = \frac{2(n_o^2 + 2)}{n_o^2 - 1} \frac{V_m}{N_A}
\]

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

\[
R_m = 4\pi\alpha_m N_A\frac{V_m}{3}
\]

With α_m in (Å3) this equation can be transformed to:

\[
R_m = 2.52\alpha_m
\]

Assuming that R_m of a glass is an additive quantity, it follows that for ternary oxide glass with a general molar formula of xB2O3.(0.35-x)BaO.65V2O5 or B2xBa0.35-xV1.3O3.6+2x it can be described by:

\[
R_m = 2.52(\Sigma a_i + N_\alpha\cdot\alpha_\alpha) =
\]

\[
= 2.52[2xa_{Ba}^+ + (0.35 - x)a_{V^{5+}}^+ + 1.3\alpha_{V^{5+}} + (3.6 + 2x)\alpha_\alpha]
\]

where \(\Sigma a_i\) denotes the molar cation polarizability given by \(2xa_{Ba}^+ + (0.35 - x)a_{V^{5+}}^+ + 1.3\alpha_{V^{5+}}\). N_\alpha denotes the number of oxide ions in the chemical formula given by (3.6+2x). \(a_{Ba}^+, \alpha_{Ba}^+, \alpha_{V^{5+}}, a_{V^{5+}}\) are the cation polarizabilities of \(\operatorname{B}^{3+} (0.002 \ \text{Å}^3), \operatorname{Ba}^{2+} (1.595 \ \text{Å}^3)\) and \(V^{5+} (0.122 \ \text{Å}^3)\)

while \(\alpha_\alpha\) is the polarizability of the oxide ion.

We have calculated the electronic oxide ion polarizability \(\alpha_\alpha\) which participate in Eq. 4 on the ground of the theoretical optical basicity \(\Lambda_m\) of B2O3 - BaO-V2O5 glasses in accordance with the approach proposed by Duffy and Ingram [11]:
\[ \Lambda_{th} = X_{B_2O_3} \Lambda_{B_2O_3} + X_{BaO} \Lambda_{BaO} + X_{V_2O_5} \Lambda_{V_2O_5} \]  

(5)

using the optical basicity data of \( BaO \) (1.15), \( B_2O_3 \) (0.42) and \( V_2O_5 \) (1.07) [12].

Eq. (5) expresses the average bulk basicity taking into account all bridging and nonbridging oxide species. In its present form it cannot estimate the changes of the cations coordination number. Regardless of these comments Eq. (5) can be used as a simple and useful formula to calculate the ideal bulk optical basicity of the glasses investigated.

The relationship between basicity and refractivity can be used as an alternative approach to optical basicity determination. On the basis of refraction data for silicates, aluminates, phosphates, borates, sulphates and some simple oxides Duffy [13] has established that an intrinsic relationship exists between electronic polarizability of the oxide ions \( a_{O^2-} \) and optical basicity of the oxide medium \( \Lambda \), as given by Eq. (6):

\[ \Lambda = 1.67(1 - \frac{1}{a_{O^2-}}) \]  

(6)

This equation provides a possibility to calculate the oxide ion polarizability of the glass on the ground of its theoretical optical basicity in correspondence with:

\[ a_{O^2-} = \frac{1.67}{1.67 - \Lambda} \]  

(7)

The oxide ion polarizability \( a_{O^2-} \) of \( B_2O_3-BaO-V_2O_5 \) glasses is determined with the application of Eq. (7) introducing the basicity data obtained through Eq.(5). It provides the estimation of \( R_m \) of the glasses on the ground of Eq.(4) taking also into account the cation polarizabilities of \( Ba^{2+} \), \( B^{3+} \) and \( V^{5+} \) mentioned above. \( V_m \) was estimated using the values of the molar mass and the density of the glasses.

The data for theoretical optical basicity, \( \Lambda_m \), the oxide ion polarizability, \( a_{O^2-} \), the density \( d \), the molar refraction, \( R_m \), and molar volume, \( V_m \), are listed in Table 1.

It is seen that the glasses possess high optical basicity (~1) and high electronic oxide ion polarizability (2.4 - 2.7 Å²).

These values are indicative of 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:

\[ n^o = \sqrt{\frac{V_m + 2R_m}{V_m - R_m}} \]  

(8)

We have estimated the theoretical refractive index, \( n^o \), of \( B_2O_3-BaO-V_2O_5 \) glasses using Eq. 8. The data are listed in Table 2, column 3. As it can be seen, the glasses possess high refractive index values in the 2.48 - 2.53 range. The results shown in Table 2 are in good agreement with the experimental data referring to thin films of \( V_2O_5 \) (\( n^o = 2.59 \)) [2].

On the other hand, Duffy [14] has obtained an empirical formula that relates the energy gap, \( E_g \), to \( R_m \) for a large number of simple oxides:

\[ E_g = 20 \left(1 - \frac{R_m}{V_m}\right)^2 \]  

(9)

We have used Eq. (9) to calculate the energy gap of \( B_2O_3-BaO-V_2O_5 \) glasses. The obtained data are presented in Table 2, column 4. As it can be seen, the glasses have a narrow energy gap in the 2.5 - 2.7 eV range. The results shown in Table 2 are in excellent agreement with experimental data for the energy gap of thin films of \( V_2O_5 \) (\( E_g = 2.5 \) eV) [2].

**Average single bond strength of the glasses**

According to the approach proposed by Dimitrov and Komatsu [10] it is possible to calculate the average single bond strength \( B_{M-O} \) of \( B_2O_3-BaO-V_2O_5 \) glasses taking into account the mole fraction of each oxide in the glass composition:

\[ B_{M-O} = xB_{B-O} + yB_{Ba-O} + (1-x-y)B_{V-O} \]  

(10)

where \( B_{B-O} \), \( B_{Ba-O} \) and \( B_{V-O} \) are single bond strengths of \( M-O \) in the corresponding individual oxide. We have determined the average single bond strength \( B_{M-O} \) of the glasses with the application of Eq. (10) using \( B_{M-O} \) values of 138 kJ mol\(^{-1}\) for \( BaO \), 498 kJ mol\(^{-1}\) for \( B_2O_3 \) and 313 kJ mol\(^{-1}\) for \( V_2O_5 \) (see Ref. 12) and taking into account the mole fraction of each oxide in the glass composition. The data obtained are presented in Table 2, column 6. It is seen that the single bond strength
increases from 255 kJ mol\(^{-1}\) to 305 kJ mol\(^{-1}\) with \(\text{B}_2\text{O}_3\) content increase and \(\text{BaO}\) content decrease. We can assume, from chemical bonding point of view, that the high \(\text{B}_{\text{M-O}}\) value about 480 - 350 kJ mol\(^{-1}\) is indicative of the average oxide ion participation in more covalent M-BO bonds such as P-O, Si-O and Ge-O. There is a strong covalent interaction between cations and oxide ions along these bonds. Those are more acidic glasses. The decrease of \(\text{B}_{\text{M-O}}\) could be attributed to formation of M-NBO or other mixed bridging bonds with increased ionicity. The smallest values of \(\text{B}_{\text{M-O}}\) about 250 kJ mol\(^{-1}\) are obtained for tellurite and bismuthate glasses [10, 15]. It is assumed that these values are connected with the presence of Te-NBO, Te-BO, Bi-O-B, Bi-O-P, Bi-O-Si and Bi-O-Ge along with Bi-O-Bi chemical bonds. The ionic contribution of those bonds is relatively large. The single bond strength of \(\text{B}_2\text{O}_3\) is large (0.15 - 0.25 Å\(^{-1}\)). The tellurite and bismuthate glasses have the lowest values of \(\Delta\) around 0.02 - 0.05 Å\(^{-1}\). Briefly, it seems that the results obtained for the interaction parameter \(\Delta\) of different oxide glasses provide a good ground for predicting the interionic interactions in multicomponent oxide glasses on the basis of their refractive index. According to this approach the interaction parameter of \(\text{B}_2\text{O}_3\)-BaO-V\(_2\text{O}_5\) glasses was calculated by us using the following equation,

\[
\Delta = X_{\text{B}_{\text{O}}} \frac{(3,921 - \alpha_{\text{O}^-})}{2(\alpha_{\text{O}^+} + 3,921)(\alpha_{\text{O}^-} + \alpha_{\text{O}^+})} + X_{\text{BaO}} \frac{(3,921 - \alpha_{\text{O}^-})}{2(\alpha_{\text{Ba}^+} + 3,921)(\alpha_{\text{O}^-} + \alpha_{\text{Ba}^+})} + X_{\text{V}_{\text{O}}} \frac{(3,921 - \alpha_{\text{O}^-})}{2(\alpha_{\text{V}^+} + 3,921)(\alpha_{\text{O}^-} + \alpha_{\text{V}^+})}
\]

where \(X_{\text{B}_{\text{O}}}\), \(X_{\text{BaO}}\) and \(X_{\text{V}_{\text{O}}}\) are the equivalent fractions based on the oxygen amount contributed by each oxide to the overall glass stoichiometry; \(\alpha_{\text{O}^-}\) is the oxide ion polarizability in the glass, while \(\alpha_{\text{O}^+}\), \(\alpha_{\text{Ba}^+}\), \(\alpha_{\text{V}^+}\) are the cation polarizabilities. The Pauling’s value of 3.921 Å\(^3\) for the free oxide ion electronic polarizability is used. The calculated data of the interaction parameter of ternary \(\text{B}_2\text{O}_3\)-BaO-V\(_2\text{O}_5\) glasses are given in Table 2 (column 5). The glasses possess small values of the

Interaction parameter of the glasses

Yamashita and Kurosawa [16] 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 aiming to take into account the effect of the charge overlapping between neighboring ions. A quantitative measure of this complex interaction is given by the so-called interaction parameter, \(\Delta\), 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 [17]. The authors have determined refractive index based interaction parameter \(\Lambda_{\text{th}}\) of various binary oxide glasses including phosphate, borate, silicate, germanate, tellurite, titanate and bismuthate [15, 18]. It is found that the interaction parameter of glasses formed by two classical glass-formers as well as conventional borate, phosphate, and silicate glasses is large (0.15 - 0.25 Å\(^{-1}\)). The tellurite and bismuthate glasses have the lowest values of \(\Delta\) around 0.02 - 0.05 Å\(^{-1}\).

Table 1. Compositions, optical basicity \(\Lambda_{\text{th}}\), oxide ion polarizability \(\alpha_{\text{O}^-}\), density \(d\), molar volume \(V_m\) and molar refractivity \(R_m\) of \(\text{B}_2\text{O}_3\)-BaO-V\(_2\text{O}_5\) glasses.

<table>
<thead>
<tr>
<th>№</th>
<th>(\text{B}_2\text{O}_3)</th>
<th>(\text{BaO})</th>
<th>(\text{V}_2\text{O}_5)</th>
<th>(\Lambda_{\text{th}})</th>
<th>(\alpha_{\text{O}^-})</th>
<th>(d)</th>
<th>(V_m)</th>
<th>(R_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>34</td>
<td>65</td>
<td>1.052</td>
<td>2.702</td>
<td>4.147</td>
<td>41.25</td>
<td>26.56</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>32</td>
<td>65</td>
<td>1.041</td>
<td>2.654</td>
<td>4.070</td>
<td>41.62</td>
<td>26.76</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>30</td>
<td>65</td>
<td>1.030</td>
<td>2.609</td>
<td>3.992</td>
<td>42.01</td>
<td>26.95</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>28</td>
<td>65</td>
<td>1.019</td>
<td>2.566</td>
<td>3.914</td>
<td>42.42</td>
<td>27.15</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>25</td>
<td>65</td>
<td>1.004</td>
<td>2.506</td>
<td>3.798</td>
<td>43.05</td>
<td>27.44</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>20</td>
<td>65</td>
<td>0.979</td>
<td>2.416</td>
<td>3.604</td>
<td>44.21</td>
<td>27.93</td>
</tr>
</tbody>
</table>
interaction parameter in the 0.051-0.072 Å⁻³ range. The interaction parameter is a quantitative measure for the interionic interaction of negative ions such as O²⁻ with the nearest neighbors (cations). A small interaction parameter means weak interionic interactions resulting in large unshared electron density at an averaged oxide ion. Since both the interaction parameter A and the 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 referring to the interaction parameter A against the data of single bond strength B_M-O of B₂O₃-BaO-V₂O₅ glasses in Fig. 1. As it is seen, a good agreement between the data based on different initial quantities is observed. A systematic increase in the interaction parameter 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 those of pure V₂O₅ (B_V-O = 313 kJ mol⁻¹ and A(no) = 0.057 Å⁻³) which means that the interaction along V-O bonds in ternary glasses have a significant effect.

**Third order nonlinear optical susceptibility of the glasses**

The third order nonlinear susceptibility χ⁽³⁾ of B₂O₃-BaO-V₂O₅ glasses was estimated by the generalized Miller’s rule:

\[
χ⁽³⁾ = [χ⁽¹⁾]^4 \times 10^{-10}, \quad \text{esu} \quad (12)
\]

where χ⁽¹⁾ is the linear optical susceptibility calculated in accordance with:

\[
χ⁽¹⁾ = \frac{(n_e^2 - 1)}{4π} \quad (13)
\]

The obtained data are presented in Table 2, column 7. B₂O₃ - BaO - V₂O₅ glasses show high values of the third order nonlinear optical susceptibility in the 0.28 – 0.35 x 10⁻¹¹ esu range, which is about 100 times larger than that of pure silica glass (2.8 x 10⁻¹⁴ esu). The obtained results are in good agreement with the experimental data obtained by Hashimoto et al. [2] for the third order nonlinear optical susceptibility of thin films of V₂O₅ (1.1 x 10⁻¹¹ esu). This means that B₂O₃ - BaO - V₂O₅ 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 $n_0$ and $E_g$ of $\text{B}_2\text{O}_3$ - $\text{BaO}$ - $\text{V}_2\text{O}_5$ glasses in Figs. 2 and 3. It is seen that $\chi^{(3)}$ increases with increasing the refractive index and decreasing the energy gap.

**Thermal stability of the glasses**

The values and compositional dependence of the glass transition temperature $T_g$ and the crystallization temperature $T_s$ of $\text{B}_2\text{O}_3$ - $\text{BaO}$ - $\text{V}_2\text{O}_5$ glasses were similar to each other. The glasses have low glass transition temperatures $T_g$ of 260°C - 280°C and crystallization temperatures $T_s$ of 292°C - 332°C. For example, the DTA and DSC curves of a glass with composition $15\text{B}_2\text{O}_3.20\text{BaO}.65\text{V}_2\text{O}_5$ are shown in Fig. 4. The results are close to the results obtained by Hayakawa et al. for binary alkaline earth vanadate glasses [19]. Therefore $\text{BaO}$ and $\text{V}_2\text{O}_5$ play a significant role in the thermal stability and crystallization behaviours of $\text{B}_2\text{O}_3$ - $\text{BaO}$ - $\text{V}_2\text{O}_5$ glasses.

**IR-spectral analysis of the glasses**

With a view to elucidate the nature of chemical bonding in the $\text{B}_2\text{O}_3$ - $\text{BaO}$ - $\text{V}_2\text{O}_5$ glasses IR-spectra of the glasses were investigated. The spectra are presented in Fig. 5. Two bands at about 1330 cm$^{-1}$ and 1240 - 1230 cm$^{-1}$ are observed in the high frequency region. According to [20] these bands could be assigned to stretching vibrations of $\text{BO}_3$ units in orthoborate and pyroborate groups. The intensity of the second band increases with $\text{B}_2\text{O}_3$ content increase, which could be related to the increase of pyroborate $\text{B}_2\text{O}_5$ groups number. Interesting changes take place in the IR-spectra bellow 1000 cm$^{-1}$. Two well defined maxima at 900 cm$^{-1}$ and 658 cm$^{-1}$ as well as a weak shoulder at around 970 cm$^{-1}$ are outlined in the IR-spectra of glasses with small $\text{B}_2\text{O}_3$ content (1-5 mol %). The shoulder is transformed in a well defined band at 977 cm$^{-1}$ - 967 cm$^{-1}$ in the spectra of glasses containing 7 - 15 mol % $\text{B}_2\text{O}_3$. The intensity of the band at 977 cm$^{-1}$ - 967 cm$^{-1}$ increases and that of the band at 900 cm$^{-1}$ decreases with increasing $\text{B}_2\text{O}_3$ content. The assignment of these bands could be made on the basis of a large number of previous results on IR spectra of crystalline and vitreous vanadate phases [21]. The band at 900 cm$^{-1}$ is assigned to stretching vibrations $V^\prime\text{O}_2$ of free $\text{VO}_2$ groups of the $\text{VO}_3$ polyhedra. Similar groups are present in the structure of the crystalline $\text{Ba(VO}_3)_2$ [22]. The appearance of the new band at 977 - 967 cm$^{-1}$ could be connected with the transformation of $\text{VO}_3$ tetrahedra into $\text{VO}_5$ bipyramids with one V=O isolated bond. It is worth noting that $\text{VO}_4$ and $\text{VO}_5$ groups are also found by $^{51}\text{V}$ NMR spectroscopic study of binary alkaline earth vanadate glasses [23]. $\text{VO}_5$ groups are formed in the structure of crystalline and vitreous $\text{V}_2\text{O}_5$. Their IR spectra show a
band at 1020 cm$^{-1}$ assigned to the vibrations of isolated V=O bonds in VO$_5$ trigonal bipyramids [24]. According to the mechanism suggested there Ba$^{2+}$ ions occupy a position between V-O-V layers and which is why they have a direct influence on the isolated V=O bonds of the VO$_5$ groups according to the scheme:

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

This leads to an elongation of the affected V=O bonds and a drop in the frequency down to 977 cm$^{-1}$ - 967 cm$^{-1}$. According to the same mechanism B$^{3+}$ ions occupy positions in the V-O-V chain itself, where some of the weaker V-O-V bonds break up to form new V-O-B bridges instead. Simultaneously, the increase of the intensity of the band at 977 cm$^{-1}$ - 967 cm$^{-1}$ and decrease of the intensity of the band at 900 cm$^{-1}$ means that the number of VO$_5$ groups increases and the number of the VO$_4$ groups decreases with B$_2$O$_3$ content increase. The low frequency band at 658 cm$^{-1}$ possesses more complicated origin. It is probably a superposition between vibrations of bridging V-O-V and V-O-B bonds as well as bending vibrations of BO$_3$ units. On the basis of the IR-spectral results obtained we present in Fig. 6 a possible model of the structure of B$_2$O$_3$ - BaO - V$_2$O$_5$ glass with high B$_2$O$_3$ content. BO$_3$, B$_2$O$_5$, VO$_4$ with two isolated VO$_2$ bonds and Ba$^{2+}$ $\cdots$ O $= V^{5+}$ chemical bonds participate in the model. Therefore, on the basis of the above pointed discussion, the high refractive index, $n_o$, and high third order nonlinear optical susceptibility, $\chi^{(3)}$, of B$_2$O$_3$ - BaO - V$_2$O$_5$ glasses could be explained with the presence in their structure of chemical bonds such as V=O, V-O, V-O-V and B-O-V with an increased ionic contribution.

**CONCLUSIONS**

B$_2$O$_3$ - BaO - V$_2$O$_5$ glasses are investigated in respect to their refractive index, band gap, oxide ion polarizability, optical basicity, interaction parameter, single bond strength and third order nonlinear optical susceptibility. It is found that the glasses possess a high refractive index...
(2.48 - 2.54), a narrow band gap (2.54 - 2.71 eV), a high oxide ion polarizability (2.41 - 2.70 Å³), a high optical basicity (1 - 1.05), a small interaction parameter (0.05 - 0.07 Å³), a small single bond strength (255 - 305 kJ mol⁻¹), and a large third order nonlinear optical susceptibility (0.28 - 0.35x10⁻¹¹ esu). Chemical bonds such as $Ba^++\cdot\cdot\cdot O = V^3+$, V-NBO (nonbridging oxygen), V-O-B and V-O-V are 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. A structural model of glasses containing $BO_x$, $B_2O_5$, VO and VO$_2$ groups is proposed. On the basis of this study it is suggested that $B_2O_3$ - $BaO$ - $V_2O_5$ glasses would be promising materials for nonlinear optics because of their high third order nonlinear optical susceptibility. Such glasses have to be searched among those of high refractive indices, small energy gaps, small interaction parameters and small single bond strengths.

Acknowledgements
This research work was supported by University of Chemical Technology and Metallurgy, Sofia, contract 11311/2014.

REFERENCES

2. T. Hachimoto, T. Yoko, Third-order nonlinear optical properties of sol-gel-derived $V_2O_5$, $Nb_2O_5$ and $Ta_2O_5$ thin films, Appl. Opt., 1995, 34, 2941-2948.