OPTICAL PROPERTIES AND CHEMICAL BONDING
OF TiO$_2$-BaO-V$_2$O$_5$ 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

ABSTRACT

Glasses of compositions $x$TiO$_2$-(35-x)BaO.65V$_2$O$_5$ (x=0, 1, 3, 5, 10, 15 and 20 mol %) are prepared using the conventional melt quenching method. XRD, DTA and DSC analysis are performed. The XRD results confirm the amorphous nature of the samples. The ternary glasses show low glass transition temperatures, $T_g$, of 228°C - 253°C and crystallization temperatures, $T_x$, of 266°C - 323°C. The density measured decreases with increase of TiO$_2$ content from 3.542 g cm$^{-3}$ to 3.287 g cm$^{-3}$. The theoretical refractive index, the electronic oxide ion polarizability, the optical basicity and the optical band gap of the glasses are calculated by the Lorentz-Lorenz equation. The glasses are found to possess a high refractive index (2.169 - 2.236), a comparatively narrow band gap (4.01 eV - 3.67 eV), high electronic ion polarizability (2.650 Å$^3$ - 2.722 Å$^3$) and high optical basicity (1.040 - 1.057). The third order nonlinear optical susceptibility $\chi^{(3)}$ is determined by the generalized Miller’s rule and the three photon model. It is found that $\chi^{(3)}$ values are in the 0.76 - 1.1 x10$^{-12}$ esu range. The average single bond strength $B_{\text{M-O}}$ and the interaction parameter $A(n_o)$ are calculated. The bond strength is found to vary from 253 kJ mol$^{-1}$ to 285 kJ mol$^{-1}$, while the interaction parameter is in the 0.050 Å$^{-1}$ - 0.055 Å$^{-1}$ range, thus suggesting the presence of weak chemical bonds. The presence of such bonds, namely Ba…O=V, V-NBO (nonbridging oxygen), V-O-Ti and V-O-V is verified by the glasses IR-spectra. 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 TiO$_4$ groups is advanced.

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

INTRODUCTION

The materials of high optical nonlinearity become of interest in science and technology of materials after the discovery of the laser in 1962. The primary focus was on the second and third order optical nonlinearity. In particular, the third order nonlinear optical materials have attract much attention because of their great importance in the field of optical, computing and information technology, as they have possible application in photonic devices for frequency generation and modulation, optical memory and optical calculation. Photonic devices operate without transformation of the input optical signal into an electronic form and are based on the change of the optical properties of the material (refractive index, absorption coefficient) in a powerful electromagnetic field. This is a great advantage of these devices for modern optical applications since such optical components operate at speeds in femto seconds of the temporary scale (approximately $10^{-15}$ s), which is 1000 times higher than those of the best electronic components which operate in the pico seconds range (approximately $10^{-12}$ s) [1]. The study of the nature of the nonlinear optical phenomena as well as the prediction of nonlinear optical properties has its own internal logic and self-importance along with the technological importance of nonlinear optical materials.
The nonlinear optical properties of V$_2$O$_5$ thin film and TeO$_2\cdot$V$_2$O$_5$ bulk glasses were recently investigated and high values of the third order nonlinear optical susceptibility $\chi^{(3)}$ were obtained [2, 3]. The values of $\chi^{(3)}$ of BaO-V$_2$O$_5$, Fe$_2$O$_3$-BaO-V$_2$O$_5$ and B$_2$O$_3$-BaO-V$_2$O$_5$ glasses were also recently predicted [4, 5]. They, based on experimental data and the generalized Miller’s rule, are rather large indicating that such glasses are interesting materials for non-linear optical devices. Similar results in respect to $\chi^{(3)}$ as well as high refractive indices have been obtained for lead vanadate amorphous thin films [6]. In addition, noncentrosymmetric vanadates Ca$_9$R(VO$_4$)$_7$ of R=Y, La-Lu and Bi demonstrate large second harmonic generation efficiency. The latter in case of Ca$_9$Bi(VO$_4$)$_7$ is about 140 times higher than that of quartz [7].

At the same time, oxide glasses of high TiO$_2$ content seem also promising materials from optical nonlinearity point of view. For example, Hashimoto et al. reported high values of the third order nonlinear optical susceptibility $\chi^{(3)}$ of TiO$_2$ thin film (0.14x10$^{-11}$ esu) and FeTiO$_3$ (0.33x10$^{-11}$ esu) [8, 9]. These were measured by THG method. The same method was applied by Terashima et al. [10] who obtained the $\chi^{(3)}$ values of different BaO-TiO$_2$-B$_2$O$_3$ glasses and established that they increase with increase of TiO$_2$ content. The highest $\chi^{(3)}$ value obtained is 22.7 x 10$^{-14}$ esu, about 8 times higher than that of pure silica glass. Recently, Kosaka et al. [11] reported data about SHG in BaO-TiO$_2$-B$_2$O$_3$ crystallized glasses.

The second harmonic intensity of the sample containing Ba$_3$Ti$_3$(BO$_3$)$_2$ crystals was found to be 68 times as high as that of $\alpha$-quartz. Abdel-Baki and El-Diasty [12] discussed the nonlinear optical properties of TiO$_2$ containing oxide glasses reported by different authors.

It is of scientific and practical interest to check the joint effect of V$_2$O$_5$ and TiO$_2$ on the optical properties of the glasses. In this connection the aim of the present study is to investigate the electronic oxide ion polarizability, that is the optical basicity, the interaction parameter and the average single bond strength of TiO$_2$-BaO-V$_2$O$_5$ glasses, to look for some intrinsic relationship between them and to predict the third order nonlinear optical susceptibility taking into consideration the structure of the glasses.

**EXPERIMENTAL**

Glasses of composition of $x$TiO$_2$.(35-$x$)BaO.65V$_2$O$_5$ ($x = 0, 1, 3, 5, 10, 15$ and $20$ mol%) were prepared by using the conventional melt-quenching method. Chemical powders of reagent grade TiO$_2$, V$_2$O$_5$ and BaCO$_3$ were mixed together and melted in a porcelain crucible at 900ºC - 950ºC in an electric furnace for 15 min. The melts were poured onto an aluminum plate and pressed to thickness of 1mm - 2 mm by another copper plate. The glasses densities were determined at room temperature by a pycnometer using distilled water as an immersion liquid. The IR-spectra of the glasses were recorded in the

<table>
<thead>
<tr>
<th>Composition</th>
<th>M (g mol$^{-1}$)</th>
<th>d (g cm$^{-3}$)</th>
<th>$V_m$ (cm$^3$ mol$^{-1}$)</th>
<th>$\Lambda_{th}$</th>
<th>$\alpha_{o2}$ (n$_0$)</th>
<th>$\alpha_m$ A$^3$</th>
<th>$R_m$ cm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1TiO$_2$.34BaO.65V$_2$O$_5$</td>
<td>171.16</td>
<td>3.542</td>
<td>48.32</td>
<td>1.057</td>
<td>2.722</td>
<td>10.59</td>
<td>26.70</td>
</tr>
<tr>
<td>3TiO$_2$.32BaO.65V$_2$O$_5$</td>
<td>169.69</td>
<td>3.517</td>
<td>48.25</td>
<td>1.055</td>
<td>2.714</td>
<td>10.62</td>
<td>26.76</td>
</tr>
<tr>
<td>5TiO$_2$.30BaO.65V$_2$O$_5$</td>
<td>168.22</td>
<td>3.489</td>
<td>48.21</td>
<td>1.053</td>
<td>2.706</td>
<td>10.65</td>
<td>26.83</td>
</tr>
<tr>
<td>10TiO$_2$.25BaO.65V$_2$O$_5$</td>
<td>164.54</td>
<td>3.483</td>
<td>48.10</td>
<td>1.048</td>
<td>2.687</td>
<td>10.71</td>
<td>27.00</td>
</tr>
<tr>
<td>15TiO$_2$.20BaO.65V$_2$O$_5$</td>
<td>160.87</td>
<td>3.349</td>
<td>48.04</td>
<td>1.044</td>
<td>2.668</td>
<td>10.78</td>
<td>27.17</td>
</tr>
<tr>
<td>20TiO$_2$.15BaO.65V$_2$O$_5$</td>
<td>157.20</td>
<td>3.287</td>
<td>47.82</td>
<td>1.040</td>
<td>2.650</td>
<td>10.85</td>
<td>27.33</td>
</tr>
</tbody>
</table>
2000 cm\(^{-1}\) - 400 cm\(^{-1}\) range by using FT-IR spectrometer Varian 600-IR. The samples for these measurements were prepared in the form of KBr–discs. The precision of the absorption maxima was \(\pm 3\) cm\(^{-1}\). The DTA and DSC curves were recorded at 10\(^\circ\)C/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 on the ground of the DSC curves. The amorphous nature of the samples was identified using X-Ray diffractometer Philips APD15 Cu \(k_\alpha\) graphite monochromator.

**RESULTS AND DISCUSSION**

**Density of the glasses**

The values of the density of the glass samples are presented in column 3 of Table 1. It shows that the increase of TiO\(_2\) content brings about density decrease from 3.542g cm\(^{-3}\) - 3.287g cm\(^{-3}\). The composition dependence is shown in Fig. 1. It is seen that almost linear relationship exists.

**X-ray diffraction analysis**

An example of X-ray diffraction pattern of 5TiO\(_2\).30 BaO.65V\(_2\)O\(_5\) glass is presented in Fig. 2. No sharp peak is observed which indicates absence of a crystalline nature. The curve shows only broad diffuse scattering at about 20 - 30 2\(\theta\) angles which is characteristic of long range disorder. This refers to the amorphous nature of the samples investigated.

**Thermal stability of the glasses**

The values as well as the composition dependence of the glass transition temperature, \(T_g\), and the crystallization temperature, \(T_x\), of TiO\(_2\)-BaO-V\(_2\)O\(_5\) glasses are close to each other. The glasses have low \(T_g\) and \(T_x\) values of 227\(^\circ\)C - 256\(^\circ\)C and 266\(^\circ\)C - 331\(^\circ\)C, correspondingly. For example, the DTA and DSC curves of the glass of composition 15TiO\(_2\).20BaO.65V\(_2\)O\(_5\) are shown in Fig. 3.

The results are close to those obtained by Hayakawa et al. for binary alkaline earth vanadate glasses [13]. This provides to conclude that BaO and V\(_2\)O\(_5\) play affect significantly the thermal stability and the crystallization behavior of TiO\(_2\)-BaO-V\(_2\)O\(_5\) glasses. At the same time the difference \(\Delta T = T_x - T_g\) (75\(^\circ\)C - 40\(^\circ\)C) is small indicating low thermal stability of these glasses. It decreases with TiO\(_2\) content increase.
Application of the polarizability approach to TiO$_2$-BaO-V$_2$O$_5$ glasses

Electronic polarizability and optical basicity of TiO$_2$-BaO-V$_2$O$_5$ glasses

The Lorentz-Lorenz equation is the most familiar and widely used relationship in the polarizability approach. It relates the molar refraction $R_m$ to the refractive index $n_o$ and the molar volume $V_m$ of the substance by,

$$R_m = \frac{n_o^2 - 1}{n_o^2 + 2} V_m$$

(1)

This equation gives the average molar refraction of isotropic substances, i.e. of liquids, glasses and cubic crystals. The molar refraction $R_m$ can be expressed as a function of molar polarizability, $\alpha_m$, in case the Avogadro’s number $N_A$ is introduced

$$R_m = \frac{4\pi\alpha_m N_A}{3}$$

(2)

With $\alpha_m$ in (Å$^3$) this equation can be transformed to,

$$R_m = 2.52 \alpha_m$$

(3)

Assuming that $\alpha_m$ of a glass is an additive term, the molar refraction of a ternary oxide glass of the general molar formula $x\text{TiO}_2(0.35-x)\text{BaO.0}65\text{V}_2\text{O}_5$ can be presented as follows,

$$R_m = 2.52(\sum \alpha_i + N\alpha_{O^-}) = 2.52(a\alpha_{Ti^{4+}} + b\alpha_{Ba^{2+}} + c\alpha_{V^{5+}} + N\alpha_{O^-})$$

(4)

where, $\alpha_{Ti^{4+}}$, $\alpha_{Ba^{2+}}$ and $\alpha_{V^{5+}}$ are the cation polarizabilities of $Ti^{4+}$, $Ba^{2+}$ and $V^{5+}$, respectively, $\alpha_{O^-}$ is the electronic oxide ion polarizability, $a$, $b$ and $c$ are numbers of the cations, while $N$ is the oxide ions number in one molecule of glass. According to [14] the cation polarizabilities are: $\alpha_{Ti^{4+}} = 0.184$ Å$^3$; $\alpha_{Ba^{2+}} = 1.595$ Å$^3$; $\alpha_{V^{5+}} = 0.122$ Å$^3$.

We have calculated the electronic oxide ion polarizability $\alpha_{O^-}$ participating in Eq. 4 on the ground of the theoretical optical basicity $\Lambda_{th}$ of TiO$_2$-BaO-V$_2$O$_5$ glasses in accordance with the approach proposed by Duffy and Ingram [15]:

$$\Lambda_{th} = X_{TiO_2}\Lambda_{TiO_2} + X_{BaO}\Lambda_{BaO} + X_{V_2O_5}\Lambda_{V_2O_5}$$

(5)

where $X_{TiO_2}$, $X_{BaO}$ and $X_{V_2O_5}$ are the equivalent fractions based on the amount of oxygen contributed by each oxide to the overall glass stoichiometry, while $\Lambda_{TiO_2}$, $\Lambda_{BaO}$ and $\Lambda_{V_2O_5}$ are the optical basicities of the individual oxides ($\Lambda_{TiO_2} = 0.97$; $\Lambda_{BaO} = 1.22$ and $\Lambda_{V_2O_5} = 1.04$ [16, 17]). Eq. 5 expresses the average bulk basicity taking into consideration all oxide bridging and nonbridging species present. It cannot estimate in its present form the coordination number of the cations changes. Irrespective of these limitations 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 appears to be an alternative approach to optical basicity determination. On the basis of refraction data for silicates, aluminates, phosphates, borates, sulphates and some simple oxides Duffy [18] found an intrinsic relationship between electronic polarizability of the oxide ions and optical basicity of the oxide medium, $\Lambda$, as given by Eq. 6:

$$\Lambda = 1.67 \left[1 - \frac{1}{\alpha_{O^-}}\right]$$

(6)

That empirical equation shows that the optical basicity increases with increase of the oxide ion polarizability. It is used for determined of optical basicity of numerous oxides and oxide glasses [14, 16, 19]. The oxide ion polarizability can be calculated on the ground of Eq. 6 with the application of:

$$\alpha_{O^-} = \frac{1.67}{1.67 - \Lambda}$$

(7)

The basicity data obtained using Eq. 5 is introduced to Eq. 7 to calculate the oxide ion polarizability of TiO$_2$-BaO-V$_2$O$_5$ glasses. The values obtained as well as those of cation polarizabilities of Ba$^{2+}$, Ti$^{4+}$ and V$^{5+}$ mentioned above provide to estimate their molar refraction $R_m$ with the application of Eq. 4. The molar volume $V_m$ is determined on the basis of the molar mass and the density of the glasses. The values of the theoretical optical basicity $\Lambda_{th}$, the oxide ion polarizability, the density $d$, the molar refraction $R_m$ and the 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 (2.650 Å$^3$ - 2.722 Å$^3$) which is indicative of their basic nature.

Refractive index and optical band gap of TiO$_2$-BaO-V$_2$O$_5$ glasses

According to the Lorentz-Lorenz equation the refractive index of the substance can be described by:

$$n_o = \sqrt{\frac{V_m + 2R_m}{V_m - R_m}}$$

(8)
We have estimated the theoretical refractive index $n_0$ of TiO$_2$-BaO-V$_2$O$_5$ glasses using Eq. 8. The data is listed in column 2 of Table 2. It is seen that the glasses possess high values of the refractive index in the 2.169 - 2.236 range. The values summarized in Table 2 are in good agreement with the experimental data concerning the refractive index of thin films of V$_2$O$_5$ ($n_0 = 2.59$); TiO$_2$ ($n_0 = 2.40$, rutile), TiO$_2$ ($n_0 = 2.29$, anatase) and FeTiO$_3$ ($n_0 = 2.33$) [2, 8, 9].

On the other hand, Duffy [20] has obtained an empirical formula that relates the energy gap $E_g$ to molar refraction $R_m$ for a large number of simple oxides,

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

(9)

We have used Eq. 9 to calculate the energy gap of TiO$_2$-BaO-V$_2$O$_5$ glasses. The data obtained is presented in column 3 of Table 2. It is seen that the glasses have narrow energy gap in the 4.01eV - 3.67 eV range. The results shown in Table 2 are in agreement with experimental data referring to the energy gap of thin films of V$_2$O$_5$ ($E_g = 2.5$ eV), TiO$_2$ ($E_g = 3eV$, rutile), TiO$_2$ ($E_g = 3.2$eV, anatase) and FeTiO$_3$ ($E_g = 2.2$ eV) [2, 8, 9].

**Chemical bonding of the glasses**

**Average single bond strength of the glasses**

It is possible to calculate the average single bond strength $B_{M-O}$ of TiO$_2$-BaO-V$_2$O$_5$ glasses on the ground of the approach proposed by Dimitrov and Komatsu [21]. The values of $B_{M-O}$ referring to the corresponding simple oxides and the mole fraction of each oxide present in the glass composition are required to be substituted in:

$$B_{M-O} = xB_{n-O} + yB_{Ba-O} + (1-x-y)B_{V-O}$$

(10)

where $B_{n-O}$, $B_{Ba-O}$ and $B_{V-O}$ are the single bond strengths of M-O in the corresponding individual oxide. We have applied Eq. 10 using $B_{M-O}$ values of 138 kJ mol$^{-1}$, 305 kJ mol$^{-1}$ and 313 kJ mol$^{-1}$ in case of BaO, TiO$_2$ and V$_2$O$_5$, correspondingly (see Ref. 22) and taking into account the mole fraction of each oxide in the glass composition. The values obtained are presented in column 4 of Table 2. It is seen that the single bond strength increases from 253 kJ mol$^{-1}$ to 285 kJ mol$^{-1}$ with TiO$_2$ content increase and BaO content decrease. From chemical bond point of view we can assume that the high value of the glass $B_{M-O}$ in the range of 480 kJ mol$^{-1}$ - 350 kJ mol$^{-1}$ is indicative of the participation of an average oxide ion in more covalent M-BO bonds such as P-O, Si-O and Ge-O. There is strong covalent interaction between the cations and the oxide ions along these bonds. Those are more acidic glasses. The decrease of $B_{M-O}$ could be attributed to the formation of M-NBO or other mixed bridging bonds of increased ionicity. The smallest values of $B_{M-O}$ of ca 250 kJ mol$^{-1}$ are obtained for tellurite and bismuthate glasses [23]. It is assumed that these values can be referred to 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 TiO$_2$-BaO-V$_2$O$_5$ glasses is close to that of tellurite and bismuthate glasses. V-NBO and V-O-Ti are most probably formed along with V-O-V chemical bonds in their structure.

**Interaction parameter of the glasses**

Yamashita and Kurosawa [24] 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 accounting for the charge overlapping effect between neighboring ions. A quantitative measure of this complex interaction is given by the so-called interaction parameter $A$, which in case of a chosen cation-anion pair is a measure of the

![Table 2. Composition, refractive index $n_0$, optical band gap $E_g$, average single bond strength $B_{M-O}$, interaction parameter $A$, metallization criterion $M(n_0)$ of the TiO$_2$-BaO-V$_2$O$_5$ glasses.](image-url)
charge overlapping between the oxide ion and its nearest positive neighbor. Dimitrov and Komatsu advanced an approach to the calculation of the interaction parameter in case of oxide glasses [19, 22]. The authors determined the refractive index based interaction parameter $A(n_0)$ of various binary oxide glasses including phosphate, borate, silicate, germanate, tellurite, titanate and bismuthate [19]. It was found that the value of the interaction parameter of glasses formed by two classical glass-formers as well as conventional borate, phosphate, and silicate glasses was high (0.15 Å$^{-3}$ - 0.25 Å$^{-3}$). The tellurite and bismuthate glasses showed the lowest values of $A$ of ca 0.02 Å$^{-3}$ - 0.05 Å$^{-3}$. It seems reasonable to accept that the values of $A$ obtained for different oxide glasses can be used to predict the interionic interactions in multicomponent oxide glasses on the basis of their refractive index. We have calculated the interaction parameter of TiO$_2$-BaO-V$_2$O$_5$ glasses following this approach. The calculation proceeded in accordance with:

$$A = X_{TiO_2} \frac{3.921 - \alpha_{O^2-}}{2(\alpha_{Ti^{4+}} + 3.921)(\alpha_{O^2-} + \alpha_{Ti^{4+}})} +$$

$$+ X_{BaO} \frac{3.921 - \alpha_{O^2-}}{2(\alpha_{Ba^{2+}} + 3.921)(\alpha_{O^2-} + \alpha_{Ba^{2+}})} +$$

$$+ X_{V_2O_5} \frac{3.921 - \alpha_{O^2-}}{2(\alpha_{V^{5+}} + 3.921)(\alpha_{O^2-} + \alpha_{V^{5+}})}$$

where $X_{TiO_2}$, $X_{BaO}$ and $X_{V_2O_5}$ are the equivalent fractions based on the amount of oxygen contributed by each oxide to the overall glass stoichiometry, $\alpha_{O^2-}$ is the electronic polarizability of the free oxide ion, $\alpha_{Ti^{4+}}$ is the oxide ion polarizability in the glass, while $\alpha_{Ti^{4+}}$, $\alpha_{Ba^{2+}}$, and $\alpha_{V^{5+}}$ are the cation polarizabilities. The Pauling’s value of 3.921 Å$^3$ for the electronic polarizability of the free oxide ion is used. The values of the interaction parameter of the ternary TiO$_2$-BaO-V$_2$O$_5$ glasses are given in column 5 of Table 2. It is seen that the considered are small in the range from 0.050 Å$^{-3}$ to 0.055 Å$^{-3}$. The interaction parameter quantifies the interionic interaction of negative ions such as O$^2-$ with the nearest neighbors (cations). The small values refer to weak 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 $A$ versus $B_{M-O}$ of TiO$_2$-BaO-V$_2$O$_5$ glasses. The dependence obtained is illustrated in Fig. 4. It shows that a good agreement could be observed between the data based on different initial quantities. A systematic increase of the interaction parameter with the composition corresponds to a systematic increase in the average single bond strength. Furthermore, the average single bond strength and the interaction parameter of the ternary vanadate glasses are close to those of pure V$_2$O$_5$ ($B_{V-O}$ = 313 kJ mol$^{-1}$ and $A(n_0)$ = 0.057 Å$^{-3}$) which means that the interaction along V-O bonds in ternary glasses has a significant effect.

**Metallization criterion**

The ratio $R_m/V_m$ is referred to as polarizability per unit volume. It can be directly determined on the ground of the Lorentz-Lorenz equation

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

According to the Herzfeld theory of metallization [25] the following simple criterion appears to be the necessary but sufficient condition to predict the metallic or insulating behavior of the condensed state [25]: $R_m/V_m > 1$ (metal) and $R_m/V_m < 1$ (insulator).

It provides to determine the nonmetal/metal behavior of the material considered. The relation expressed by:

$$M(n_0) = I \cdot \frac{R_m}{V_m}$$

is known as the metallization criterion [26]. Materials of $M$ close to 1 are typical insulators. On the contrary,
M values close to zero indicate that the width of both valence and conduction bands is large, which in turn results in a narrow band gap and increased metallicity of the solid. Dimitrov and Sakka [14] and Dimitrov and Komatsu [19] calculated the metallization criterion for a large number of simple oxides and binary oxide glasses. It was found that oxides of a high refractive index and a small energy gap such as PbO, TiO$_2$, Sb$_2$O$_3$, etc. possess a metallization criterion in the 0.35 - 0.45 range, while alkaline and alkaline-earth oxides as well as B$_2$O$_3$ and SiO$_2$ have a small refractive index, large energy gap and metallization criterion in the 0.50 - 0.70 range. Similarly, tellurite glasses containing Nb$_2$O$_5$, TiO$_2$, 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. The small metallization criterion means increased tendency for metallization of the glasses. We calculated the metallization criterion for TiO$_2$-BaO-V$_2$O$_5$ glasses and the data obtained is presented in column 6 of Table 2. It is seen that the metallization criterion decreases from 0.448 to 0.428 with increase of TiO$_2$ content. The values obtained showed also that TiO$_2$-BaO-V$_2$O$_5$ glasses are close to tellurite and lead-titanate glasses, i.e. they show an increased tendency to metallization.

**IR-spectra of the glasses**

The IR-spectra of TiO$_2$-BaO-V$_2$O$_5$ glasses were investigated aiming to elucidate the nature of chemical bonding there. The spectra are presented in Fig 5. Two well defined maxima at 903 cm$^{-1}$ and 651 cm$^{-1}$ - 647 cm$^{-1}$, a shoulder at 743 cm$^{-1}$ and a weak maximum at 453 cm$^{-1}$ - 449 cm$^{-1}$ as well as a weak shoulder at around 970 cm$^{-1}$ are outlined in the IR spectra of 35BaO-65V$_2$O$_5$ and glasses of a small TiO$_2$ content (1mol % - 3mol %). The shoulder is transformed into a well-defined band at 978 cm$^{-1}$ - 970 cm$^{-1}$ in the spectra of glasses containing 5 mol % - 20 mol % TiO$_2$. The intensity of the band at 978 cm$^{-1}$ - 970 cm$^{-1}$ increases and that of the band at 900 cm$^{-1}$ decreases, whereas the band shifts to lower frequencies up to 881 cm$^{-1}$ with TiO$_2$ content increase. At the same time the shoulder at 743 cm$^{-1}$ disappears in the spectra of the glasses containing 5 mol % - 20 mol % TiO$_2$. The assignment of these bands is made on the ground of the presence of different vanadium-oxygen groups in the structure and their vibrations in correspondence with the IR spectra results referring to crystalline and vitreous vanadate phases [27 - 34]. According to the structural $^{51}$V NMR studies of the structure of alkaline earth vanadate glasses performed by Hayakawa et al [35] the structure of the glasses containing less than 45 mol % MO (M=Ca, Sr and Ba) is characterized by at least four kinds
of vanadate groups: (i) V\textsubscript{2}O\textsubscript{7}; (ii) (VO\textsubscript{3})\textsubscript{n}-single chains; (iii) (V\textsubscript{2}O\textsubscript{8})\textsubscript{n}-zigzag chains constituted of VO\textsubscript{5} trigonal bipyramids and (iv) condensed VO\textsubscript{4} tetrahedral groups which are different from the (VO\textsubscript{3})\textsubscript{n}-single chain found in crystalline Ba(VO\textsubscript{3})\textsubscript{2} [35]. On this basis the band at around 900 cm\textsuperscript{-1} is assigned to symmetrical stretching vibrations $\nu_{V=O}^{ss}$ of free VO\textsubscript{2} groups of VO\textsubscript{4} tetrahedra from (VO\textsubscript{3})\textsubscript{n} chains and $\nu_{V=O}^{ss}$ of free VO\textsubscript{3} groups of VO\textsubscript{4} tetrahedra from V\textsubscript{2}O\textsubscript{7} units, while the band at 743 cm\textsuperscript{-1} could be attributed to asymmetrical stretching vibrations $\nu_{V=O}^{as}$ of these tetrahedra. The appearance of a new band at 978 cm\textsuperscript{-1} - 970 cm\textsuperscript{-1} could be connected with the transformations of VO\textsubscript{4} tetrahedra into VO\textsubscript{5} trigonal bipyramids with one V=O isolated bond. Similar transformation of VO\textsubscript{4} into VO\textsubscript{5} groups has been observed in the structure of V\textsubscript{2}O\textsubscript{5}-Bi\textsubscript{2}O\textsubscript{3}-ZnO glasses with Bi\textsubscript{2}O\textsubscript{3} content increase [31]. VO\textsubscript{5} groups are formed in the structure of crystalline and vitreous V\textsubscript{2}O\textsubscript{5}. Their IR spectra show a band at 1020 cm\textsuperscript{-1} assigned to the vibrations of isolated V=O bonds in VO\textsubscript{5} trigonal bipyramids [28]. According to the mechanism suggested in ref. [28] Ba\textsuperscript{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\textsubscript{5} groups according to the scheme: Ba\textsuperscript{2+}… O=V\textsuperscript{5+}

This leads to an elongation of the affected V=O bonds and a drop in the frequency down to 978 cm\textsuperscript{-1} - 970 cm\textsuperscript{-1}. Simultaneously, the increase of the intensity of the band at 978 cm\textsuperscript{-1} - 970 cm\textsuperscript{-1} and the decrease of the intensity of the band at around 900 cm\textsuperscript{-1} means that the number of VO\textsubscript{5} groups increases, while the number of the VO\textsubscript{4} groups decreases with TiO\textsubscript{2} content increase. The shift of the band at 903 cm\textsuperscript{-1} to lower frequencies up to 881 cm\textsuperscript{-1} could be explained with formation of V-O-Ti bridging bonds created by the effect of Ti\textsuperscript{4+} ion on the non-bridging oxygen from VO\textsubscript{2} groups. Similar vibration at about 865 cm\textsuperscript{-1} has been observed in the crystalline spectra of ZnV\textsubscript{2}O\textsubscript{6} and CdV\textsubscript{2}O\textsubscript{6}. This band could be assigned to the vibrations of Zn(Cd)-O-V bonds [29]. We assume that TiO\textsubscript{4} groups are formed in the structure of the glasses. The frequencies of isolated TiO\textsubscript{4} are at 750 cm\textsuperscript{-1}[36]. When they are polymerized the frequencies of TiO\textsubscript{4} stretching modes would be expected to increase up to 910 cm\textsuperscript{-1} - 880 cm\textsuperscript{-1}. According to ref. [32] the band at 651 cm\textsuperscript{-1} could be assigned to asymmetrical stretching vibrations $\nu_{V-O-Ti}^{as}$, while the band at 449 cm\textsuperscript{-1} is attributed to the bending vibrations $\delta_{V-O}$ of the VO bonds [34]. On the basis of the IR spectral results obtained we elaborated the structural model of glass of high TiO\textsubscript{2} content containing VO\textsubscript{4}, VO\textsubscript{5} and TiO\textsubscript{4} groups. V-O-V, V-O-Ti and Ba\textsuperscript{2+}…O=V\textsuperscript{5+} chemical bonds are formed between the groups. It is illustrated in Fig. 6.

![Fig. 6. Structural model for glass with high TiO\textsubscript{2} content.](image-url)
The third order nonlinear susceptibility $\chi^{(3)}$ of TiO$_2$-BaO-V$_2$O$_5$ glasses is estimated following the generalized Miller’s rule

$$\chi^{(3)} = \left[\chi^{(1)}\right]^3 \cdot 10^{-10} \, \text{esu}$$  \hspace{1cm} (14)

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

$$\chi^{(1)} = \left(\frac{n_0^2 - 1}{4\pi}\right)$$  \hspace{1cm} (15)

and the three photon model described by:

$$\chi^{(3)} = \frac{\Phi}{(E_g - 3\omega)(E_g - 2\omega)(E_g - \omega)}$$  \hspace{1cm} (16)

where $\Phi$ is a constant equal to 1.4.10$^{-11}$, $\omega$ is the frequency, while $E_g$ is the optical band gap.

The data obtained is presented in columns 2 and 3 of Table 3. TiO$_2$-BaO-V$_2$O$_5$ glasses show high values of the third order nonlinear optical susceptibility in the 0.76-1.1x 10$^{-12}$ esu range, which is about 100 times larger than that of pure silica glass (2.8x10$^{-14}$ esu). It is seen that good agreement exists between the refractive index $n_o$ and the energy gap $E_g$ of TiO$_2$-BaO-V$_2$O$_5$ glasses. They are illustrated in Figs. 7 and 8. It is seen that $\chi^{(3)}$ increases with increase of the refractive index and decrease of the energy gap, i.e. similar results are obtained for the glasses studied here. The high values of the third order nonlinear optical susceptibility of TiO$_2$-BaO-V$_2$O$_5$ glasses are attributed to the presence of V-O-Ti, V-O-V and Ba$^{2+}$…O=V$^{5+}$ bonds in their glass structure. Such bonds are confirmed by the IR spectra. The high electronic polarizability of the oxide ions in these bonds is most probably responsible for the high nonlinearity of the glasses.

CONCLUSIONS

Ternary TiO$_2$-BaO-V$_2$O$_5$ glasses are subjected to XRD, DTA and DSC analysis. The XRD results verify...
the amorphous nature of the samples. The DTA and DSC data shows that the glasses possess low glass transition temperatures, $T_g$, of 228°C - 253°C and crystallization temperatures, $T_x$, of 266°C - 323°C. The experimental density is found to be in the 3,287 - 3,542 g cm$^{-3}$ range. The polarizability approach based on the Lorentz-Lorenz equation is applied to TiO$_2$-BaO-V$_2$O$_5$ glasses. The electronic ion oxide polarizability, the optical basicity and the optical band gap of the glasses are calculated aiming to elucidate their theoretical refractive index. It is found that the glasses have a high refractive index (2,169 - 2,236), a comparatively narrow band gap (4,01 eV - 3,67 eV), high electronic ion polarizability (2,650 Å$^3$ - 2,722 Å$^3$) and high optical basicity (1,040 - 1,057). The theoretical third order nonlinear optical susceptibility $\chi^{(3)}$ is determined. The values obtained are in the 0.76 - 1.1x10$^{-12}$ range. It is also found that the glasses have small single bond strength and interaction parameter, thus suggesting the presence of weak chemical bonds. The presence of such bonds, namely V-O-Ti, V-O-V and Ba$^{2+}$…O=V$^{5+}$ is verified by the IR spectral analysis carried out. 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 glass of high TiO$_2$ and presence of VO$_4$, VO$_5$ and TiO$_4$ groups is advanced.

**Acknowledgements**

The authors would like to thank Dr. Sasho Vassilev from the IEES of the Bulgarian Academy of Science for carrying out the XRD measurements envisaged.

**REFERENCES**

2. T. Hashimoto, T. Yoko, Third-order nonlinear optical properties of sol-gel-derived V$_2$O$_5$, Nb$_2$O$_5$ and Ta$_2$O$_5$ thin films, Appl. Opt., 34, 1995, 2941-2948.
27. V. Dimitrov, Y. Dimitriev, Structural analysis, UCTM, Sofia, 2009, (in Bulgarian).