Structure and dielectric behaviour of glasses in the TeO$_2$-BaO-V$_2$O$_5$ system

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Abstract. The rapid development of telecommunication and information technology aims to design and investigate new functional materials. Glasses in the TeO$_2$-BaO-V$_2$O$_5$ system seem to be promising materials within this purpose. In this connection the structure and dielectric properties of the glasses have been studied. Small polaron hopping of V$^{4+}$ to V$^{5+}$ ion in the vanadate chains and the influence of BaO and TeO$_2$ on the dielectric permittivity, dielectric losses and frequency depended conductivity of the glasses measured at room temperature in the frequency range from 100 Hz to 1 MHz have been discussed.

1. Introduction

Tellurite and vanadate glasses have attracted attention because of their combination of various properties, such as semiconducting, transport, memory and threshold switching, nonlinear optical properties, etc. [1-5]. The theory of small polaron, proposed by Mott [6] turned out to be the most appropriate for interpreting the electrical conductivity behaviour of transition metal containing glasses. The hopping of a small polaron exhibit adiabatic or non-adiabatic character depending of the V$_2$O$_5$ content [2, 7-10]. The structure of TeO$_2$-V$_2$O$_5$ glasses have been investigated by means of X-ray diffraction [11], Infrared spectroscopy [12] and $^{125}$Te and $^{51}$V NMR spectroscopy [13]. It was found that with increasing V$_2$O$_5$ content, the O coordination environment of Te atoms change from the TeO$_4$ trigonal bipyramid (tbp) to the TeO$_3$ trigonal pyramid (tp), and TeO$_4$ tbp without a non-bridging oxygen (NBO) decreases, while those of TeO$_4$ tbp with an NBO and TeO$_3$ tp with two NBOs increases. The fractions of VO$_4$ tetrahedral increase and the fractions of VO$_4$ tbp decrease with increasing V$_2$O$_5$ content. The structure of TeO$_2$-BaO and V$_2$O$_5$-BaO glasses have been also investigated [12, 14-16]. The addition of BaO in the TeO$_2$-BaO glasses leads to transformation of TeO$_3$ structural groups into TeO$_3$ groups and beyond 40 mol % BaO, only TeO$_3$ groups are observed. In the case of V$_2$O$_5$-BaO glasses, when BaO content is less than 40 mol % the formation of V$_2$O$_5$-rich phase having three dimensional arrangements of branched VO$_4$ – groups are caused. On the other hand, the BaO-rich phases, Ba(VO$_3$)$_2$ are composed of (V$_2$O$_5$)$_n$ zigzag chains. Sen and Ghosh [17] have studied electrical properties of barium vanadate glasses. They have found that in the case of BaO-V$_2$O$_5$ glasses the multiphonon assisted hopping of electrons with strong interaction with optical as well as acoustical phonons is the dominant transport mechanism in these glasses.
The aim of the present work is to study the dielectric behavior of TeO2-BaO-V2O5 glasses and to investigate the impact of the BaO and TeO2 on the vanadate chains to control electro-optical phenomena.

2. Experimental
Glasses with compositions xTeO2 - (35-x) BaO - 65V2O5 (where x= 5, 10, 15, 20, 25 and 30 mol %) were prepared using a conventional melt quenching method [18]. The glass compositions are given in table 1. Reagent grade commercial powders of TeO2, BaCO3, 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. Powder X-ray diffraction patterns were collected within the range from 10 to 80° 2θ with a constant step 0.03° 2θ and counting time 52.5 sec./step on Bruker D8 Advance diffractometer (Germany) with Cu Kα radiation and Lynx Eye detector. The experimental density was measured by Archimedes method by using analytical scale Mettler Toledo New Classic ME 104 equipped with density kit. The IR spectra are recorded in the 2000 - 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 ±3 cm-1. The dielectric measurements were done on Impedance spectrometer Zanner CM6.

3. Results and discussion
3.1. Structure of the glasses
3.1.1. Density and molar volume
The density and the molar volume of the glasses was published in previous work concerning the polarization state, structure and nonlinear optical characteristics of xTeO2. (35-x)BaO.65V2O5 glasses (x=5, 10, 15, 20, 25, and 30 mol%) glasses [18]. Glasses possess density in the 3.608-3.502 g/cm³ range (table 1, column 2). Small decrease in the densities of the glasses is observed with increasing TeO2 content. It is seen also that the density of glasses with small concentration of TeO2 (up to 10 mol%) possess almost the same values. Further addition of TeO2 leads to evident density decrease [18]. The molar volume \( V_m \) was estimated by the following equation:

\[
V_m = \frac{\sum x_i M_i}{d_i}, \text{ cm}^3/\text{mol}
\]  

where \( x_i \) is the molar fraction of each component \( i \), \( M_i \) is the molar mass of \( d_i \) is an experimental data of the density. The results are presented in table 1, column 4. It is seen that the molar volume increases with increasing TeO2 content (figure. 1). The increasing in the molar volume from 47.73 cm³/mol to 49.62 cm³/mol indicates an increase in free volume with decreasing BaO content.

3.1.2. Oxygen packing density and atomic packing density
With the aim of more detailed analysis of the structure of the glasses, the oxygen packing density, \( OPD \), and the atomic packing density \( Cg \) of the glasses are estimated in the present study. The oxygen packing density is calculated, by:

\[
OPD = 1000 . N_{O_2} \cdot \frac{d_i}{M_i}
\]  

where \( N_{O_2} \) is the number of oxygens per formula units. The results are presented in table 1, column 5. The oxygen packing density as a function of the composition is shown in figure 1. It is seen that the \( OPD \) increases with increasing TeO2 content (or decrease of BaO content). The increasing of the oxygen packing density could be due to formation of more rigid and highly cross-linked network resulting in a tightly packed glass network [19] and the fact that the substitution of BaO by TeO2 increases the number of oxygen atoms in the ratio 2/1 [20].
The atomic packing density $C_g$ is defined as the ratio between the theoretical volume occupied by the constituting ions and the effective volume of the glass [21]. For multicomponent glass $C_g$ is written as

$$C_g = \frac{4 \pi N_A \sum f_i (ar^2 + br^3)}{\sum f_i M_i},$$

where $\rho$ is the glass density, $N_A$ is the Avogadro number, and $f_i$ is the molar fraction of the $i^{th}$ component having chemical formula $A_{a}B_{b}$, molar mass $M_i$, and ionic radii $r_A$ and $r_B$ for atoms A and B, respectively. Since the ionic radius depends on the local coordination environment, we need to consider the changes of the coordination numbers in vanadate glasses for $C_g$ to represent the atomic packing density of the glass as accurately as possible.

Table 1. The glass compositions, density $d$, molar mass $M$, molar volume $V_m$, oxygen packing density (OPD), $N'4(VO_4)$ fractions, $N'5(VO_5)$ fractions, atomic packing density ($C_g$).

| Composition       | Density, $d$, g/cm$^3$ [18] | M, g/mol [18] | $V_m$, cm$^3$/mol [18] | OPD | $N'_4$ (VO$_4$) | $N'_5$ (VO$_5$) | $C_g$ |
|-------------------|------------------------------|---------------|------------------------|-----|-----------------|-----------------|-------|
| 35BaO.65V$_2$O$_5$ [14] | 0.47 [13]                   | 0.53 [13]     | 0.561                  |     | 0.73 [14]       | 0.27 [14]       | 0.573  |
| 5TeO$_2$.30BaO.65V$_2$O$_5$ | 3.608                        | 172.20        | 47.73                  | 76.48 | 0.69            | 0.31            | 0.573  |
| 10TeO$_2$.25BaO.65V$_2$O$_5$ | 3.607                        | 172.51        | 47.83                  | 77.36 | 0.66            | 0.34            | 0.573  |
| 15TeO$_2$.20BaO.65V$_2$O$_5$ | 3.593                        | 172.83        | 48.10                  | 77.96 | 0.62            | 0.38            | 0.571  |
| 20TeO$_2$.15BaO.65V$_2$O$_5$ | 3.560                        | 173.14        | 48.64                  | 78.13 | 0.58            | 0.42            | 0.566  |
| 25TeO$_2$.10BaO.65V$_2$O$_5$ | 3.528                        | 173.46        | 49.17                  | 78.31 | 0.54            | 0.46            | 0.561  |
| 30TeO$_2$. 5BaO.65V$_2$O$_5$ | 3.502                        | 173.77        | 49.62                  | 78.60 | 0.51            | 0.49            | 0.557  |
| 35TeO$_2$.65V$_2$O$_5$ [13] | 3.478                        | 174.09        | 49.27                  | 78.90 | 0.47            | 0.53            | 0.554  |

According to the IR spectra of the glasses [18] no shift of the position of the band at 670 cm$^{-1}$ is observed. The band has been assigned to the degenerate stretching vibrations $\nu_{as}$ of TeO$_3$ of TeO$_3$ trigonal pyramids. The band at 902-888 cm$^{-1}$ has been assigned to the symmetrical stretching vibrations $\nu_{s}(VO_2)$ of free VO$_2$ groups of the VO$_4$ tetrahedra from -V-O-V- chains. The presence of the band at 965-978 cm$^{-1}$ could be connected with stretching vibration of non-bridging V=O bond from VO$_3$ trigonal bipyramids. The increase of the intensity of the band at 965-978 cm$^{-1}$ and decrease of the intensity of the band at 902-888 cm$^{-1}$ means that the number of VO$_3$ groups increases and the number of VO$_4$ groups decreases with increasing TeO$_2$ content and decreasing BaO content [18]. The observed change in the VO$_4$ to VO$_3$ structural groups is gradual.

Figure 1. Molar volume and oxygen packing density of the glasses as a function of TeO$_2$ content.

Figure 2. Molar volume and atomic packing density of the glasses as function of TeO$_2$ content.
Sakida et al. [13] have investigated the structure of TeO\textsubscript{2}-V\textsubscript{2}O\textsubscript{5} glasses by means of \textsuperscript{125}Te and \textsuperscript{57}V static NMR. According this study the structure of 2TV is built by N\textsubscript{4}(TeO\textsubscript{4}) = 55\%, N\textsubscript{3}(TeO\textsubscript{3}) = 45\%, N\textsuperscript{'}\textsubscript{4} (VO\textsubscript{4}) = 39\% and N\textsuperscript{'}\textsubscript{5}(VO\textsubscript{5}) = 61\%. Hayakawa et al. [14] has been investigated the structure of alkaline earth vanadate glasses xMO.(100-x)V\textsubscript{2}O\textsubscript{5} (M=Ca, Sr, Ba, x=30, 40, 45, 50, 55 mol\%) by means of \textsuperscript{51}V static and magic angle spinning (MAS) NMR spectroscopies. They have found that the structure of alkaline earth vanadate glasses consist mainly of VO\textsubscript{4} – tetrahedra and for x \leq 45 \% and the decrease of the MO content yields a mixture of the V\textsubscript{2}O\textsubscript{5} rich phase constituted of three dimensionally branched VO\textsubscript{4} groups and the MO rich phase constituted of the VO\textsubscript{5} trigonal bipyramids, followed by the decrease of (VO\textsubscript{3})\textsubscript{n} - single chains. The fractions of these vanadate groups are as follows: N\textsuperscript{'}\textsubscript{4}(VO\textsubscript{4}) = 73\% and N\textsuperscript{'}\textsubscript{5}(VO\textsubscript{5}) = 27\%, respectively. On the basis of the IR and NMR spectroscopic studies, the following conclusions could be made: the basic structural groups of TeO\textsubscript{2} in the glasses’ structure is TeO\textsubscript{3}, and a change of VO\textsubscript{4} to VO\textsubscript{5} structural groups of the V\textsubscript{2}O\textsubscript{5} with addition of TeO\textsubscript{2} is observed. Assuming that the change in the VO\textsubscript{n} groups is gradual, the fractions of VO\textsubscript{4} groups at certain composition scales with the TeO\textsubscript{2} content, and leads to N\textsuperscript{'}\textsubscript{4}(VO\textsubscript{4}) = - 0.7429x +73.

On that basis the fraction of the VO\textsubscript{5} groups for the glasses in the present study xTeO\textsubscript{2}.(35-x)BaO.65V\textsubscript{2}O\textsubscript{5} are estimated and the obtained values are presented in Table 1, Column 6 and 7. This structural change will result in the increase of V effective radius, concerning that \( r_{V^5+}^{(e)} = 0.355 \text{ Å} \) and \( r_{V^5+}^{(e)} = 0.460 \text{ Å} \) [22]. The effective radius of Te\textsuperscript{4+} for TeO\textsubscript{3} is \( r_{Te^{4+}}^{(e)} = 0.520 \text{ Å} \) and for Ba\textsuperscript{2+} is \( r_{Ba^{2+}}^{(e)} = 1.350 \text{ Å} \) [22], the Pauling value of the ionic radius of oxygen (\( r_{O^{2-}} \)) is used. The obtained results of (3) are given in table 1, column 8. It is seen that decrease in the atomic packing density for glasses with more than 10 mol\% TeO\textsubscript{2} is observed. The atomic packing density as a function of the composition is given in figure 2.

3.2. Dielectric properties

The dielectric properties as dielectric permittivity (figure 3 and figure 4), dielectric losses (figure 5), and frequency depended conductivity (figure 6) of the samples were measured at room temperature in the frequency range from 100 Hz to 1 MHz.

With increasing TeO\textsubscript{2} content (above 5 mol \%), the real part of dielectric permittivity possesses the ability to decrease and more and less stable behaviour in all frequency range (figure 4). At the same time, imaginary part of dielectric permittivity in Figure 5 and losses in Figure 6 demonstrate huge resonance process due to TeO\textsubscript{2} content.

According to the structural analysis made above, the increasing of TeO\textsubscript{2} content leads to change of the structural units on three different ways: 1) When TeO\textsubscript{2} content increases, the VO\textsubscript{4} groups decrease and VO\textsubscript{5} structural groups increase. The presence of bonds such as Te-O-V=O, V-O-V in the glass structure was established. These bonds are with weak, predominantly ionic character [18]. 2) On the other side, the increasing of TeO\textsubscript{2} content leads to form more TeO\textsubscript{3} structural groups which could be linked in the (V2O8)n zig zag chains and to deform the chains. 3) The substitution of BaO with TeO\textsubscript{2} cause more compact structure and forming linkages between the species became more probable.

In the case of those three different types of structural unit changes, the frequency depended resonance, dielectric losses and conductivity spectra could be interpreted. When TeO\textsubscript{2} content is less than 10 mol \%, the number of the isolated TeO\textsubscript{3} groups is increased in the volume and the influence of VO\textsubscript{4} groups on the electrical behaviour is dominant. Addition of TeO\textsubscript{2} more than 10\%, leads to transformation of VO\textsubscript{4} groups to VO\textsubscript{5} structural groups. At the same time, replacing of BaO with TeO\textsubscript{2} lead to increase of the oxygen packing density and the molar volume, as well as decrease in the atomic packing density. Increased number of Te-O-V bonds, and decreased effect of Ba\textsuperscript{2+}…O=V bonds in the glass structure could be the reason for the decreasing of the dielectric losses.
4. Conclusions

With addition of TeO₂, three different types of structural changes in the glass samples in system TeO₂-BaO-V₂O₅, are observed. These structures changes impact on frequency depended dielectric parameters:

1) When TeO₂ content is less than 10 mol %, the Ba²⁺ ions are distributed in interstitial sites and interact directly V-O isolated bonds (Ba²⁺…O=V), while Te⁴⁺ ions are incorporated in the chains and influence indirectly V-O bonds (O=V-O-Te).

2) In the glass volume, the single Te-O deformed bonds increase. When the TeO₂ is more than 10%, the VO₄ groups starts change to VO₅ structural groups.

3) Replacing of BaO with TeO₂ leads to form Te-O-V bonds, in the glass structure which results in decreasing of the dielectric losses. Breaking of the deformed Te-O bridges between VO₄ groups starts change to VO₅ structural groups.

The present work shows one way to control the dielectric properties caused by substitution of BaO with TeO₂ in several vanadate glasses, which could make a contribution to create promising new vitreous materials in TeO₂-BaO-V₂O₅ system with possible application in different fields of technology.
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