Nature of conductivity in $x\text{Na}_2\text{O}-(90-x)\text{V}_2\text{O}_5-10\text{P}_2\text{O}_5$ glasses: experimental study and computer simulation

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Abstract. A series of $10\text{P}_2\text{O}_5-x\text{Na}_2\text{O}-(90-x)\text{V}_2\text{O}_5$ ($x=1–5$ mol.%$) glasses was obtained by melt-quenching technique. Their thermal properties were studied using differential scanning calorimetry. The density was measured by picnometry. A combination of electrochemical techniques shows that conductivity in these glasses has an electronic nature. The conductivity passes through a maximum at 1 mol% of Na$_2$O. The model of the glass structure was constructed with non-constant force field molecular dynamics with self-assembly. The molecular dynamics simulation shows that the value of conductivity correlates with the mean coordination number for the V…V pair.

1. Introduction

Despite the fact that semiconducting glasses have been known for a long time, they still attract significant scientific attention due to numerous areas of their possible application and unsolved issues connected with their structure. In terms of electrochemical applications, vanadium glasses and glass-ceramics are believed to be promising candidates for electrode materials of lithium-ion batteries due to its high electrical conductivity [1-4].

Since the conductivity of vanadate glasses is provided by electron hops between $V^{4+}$ and $V^{5+}$ cations, one can conclude that the conductivity increases with growth of vanadium content and vice versa, the introducing of constant valence elements decreases the conductivity, as observed in [5]. Nevertheless, the substitution of vanadium by other elements may lead to an increase in conductivity for some systems. So, doping of crystalline $\text{V}_2\text{O}_5$ with Li$_2$O or Na$_2$O gives an increment in conductivity [6]. The reason for such behavior might be the stabilization of minor oxidation degree or some structural changes. For example, it was shown that the addition of bismuth oxide in vanadate glasses convert VO$_4$ groups into VO$_5$ [7].

The aim of this work is to establish effect of Na$_2$O doping on conductivity of vanadate-phosphate glasses and explain it in terms of microstructure. To obtain microscopic model of the glass we used non-constant force field molecular dynamics with self-assembly, similar to our previous work [8].

2. Experimental

Glasses in $10\text{P}_2\text{O}_5-x\text{Na}_2\text{O}-(90-x)\text{V}_2\text{O}_5$ ($x = 1–5$ mol.%) system were obtained by quenching of melt held at 950°C for 1 h between stainless steel plates. Before melting, batch was prepared by mixing of appropriate amounts of ammonium phosphate ((NH$_4$)$_2$HPO$_4$, 99.9%), vanadium oxide (V$_2$O$_5$, 99.9%), and sodium carbonate (Na$_2$CO$_3$, 99.99%); melting was conducted in platinum crucibles. After
quenching, the obtained samples were annealed at a temperature 50°C below glass transition temperature ($T_g$).

Differential scanning calorimetry (DSC) was used for determination of glass transition and crystallization temperatures. The measurements were carried out in a temperature range of 25–600 °C with a heating rate of 10 °C·min$^{-1}$ in dry Ar atmosphere using a 204 F1 Phoenix calorimeter (NETZSCH, Germany). All characteristic temperatures were determined with Proteus software (NETZSCH, Germany) with the accuracy of ± 1 °C.

To verify that obtained samples are amorphous and homogeneous and their chemical composition after melting corresponds to the nominal one, studies were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive analysis (EDX), and atomic emission spectroscopy (AES) with inductively coupled plasma. XRD measurements were conducted using a D/Max 2200 diffractometer (Rigaku, Japan) with Cu-Kα-radiation ($\lambda=1.5418$ Å) in a 2θ range of 15–55°. SEM and EDX studies were performed using a MIRA 3 LMU microscope (TESCAN, Czech Republic) equipped with an INCA Energy 350 X-max 80 (Oxford Instruments, Great Britain) system of energy-dispersive X-ray spectroscopy (EDX). Chemical composition was checked using an Optima 4300 DV (Perkin Elmer, USA) spectrometer; accuracy was 2–3%.

Liquid picnometry was used to determine the density of samples in standard 10 mL picnometers. Isopropyl alcohol was used as an immersive liquid because glasses appeared to be unstable in distilled water and purified kerosene.

Glass structure was studied by Raman spectroscopy at the room temperature using a U 1000 (Renishaw, United Kingdom) microscope-spectrometer. Raman spectra were collected from preliminary polished glass surface in a range of 4000–50 cm$^{-1}$ with a spectral resolution of 1 cm$^{-1}$; laser with a wavelength of 532 nm was used.

Since sodium ions can contribute to the total conductivity of studied glasses, two independent methods were used: impedance spectroscopy (IS) and current interrupt (CI) method, which allows one to separate contribution of electronic conductivity to the total one. Before measurements, the samples were polished and covered with a thin (50 nm) layer of Pt as an electrode. The conducted measurements were carried out using a ZIVE MP2 (WonATech, South Korea) potentiostat/galvanostat. Impedance spectra were collected in a frequency range of 0.1–100000 Hz.

Molecular dynamics simulations of the 10P$_2$O$_5$–xNa$_2$O–(90-x)V$_2$O$_5$ glasses were performed with CUDA version of aztot MD software [9]. The software, user manual, and examples of input files can be downloaded at http://aztotmd.ru/set.php?lang=en. The simulated systems consisted of about 3400 atoms (depending on the composition) placed into a cubic box of a volume corresponding to the measured molar volume. 10% of all vanadium ions were assigned tetravalent. The initial configurations including atom coordinates, lists of valent bonds and angles were obtained with self-assembly procedure, as described in [8]. After the self-assembly, the main part of the simulation was conducted with force field parameters from [10] and [8] for Na…Na and Na…O pair potentials. The systems evolved during $3'000'000$ timesteps with timestep value of $10^{-3}$ ps. Electrostatics was calculated using the assumption from [11]. Simulation temperature was controlled by the Nose-Hoover thermostat around 298 K.

3. Results and Discussion

3.1. Characterization

The absence of spontaneous crystallization in 10P$_2$O$_5$–xNa$_2$O–(90-x)V$_2$O$_5$ glasses was confirmed by XRD results presented in figure 1. No peaks corresponding to crystalline phases are observed, and XRD patterns are halo typical for amorphous substances. To confirm chemical composition of the synthesized glasses, atomic emission spectroscopy was carried out (table 1). It is seen that both nominal and real compositions are in a good agreement. Uniformity of element distribution and the absence of liqation areas as well as crystallites were checked by SEM and EDX studies. According to
the results of XRD, SEM, EDX and AES analyses, it can be concluded that the glass of the given composition without any crystalline inclusions or microinhomogeneities were obtained.

![XRD patterns](image)

**Figure 1.** XRD patterns of 10P$_2$O$_5$–xNa$_2$O–(90-x)V$_2$O$_5$ glasses.

**Table 1.** Compositions of 10P$_2$O$_5$–xNa$_2$O–(90-x)V$_2$O$_5$ glasses according to AES data (mol%).

| x, mol. % | P$_2$O$_5$ | V$_2$O$_5$ | Na$_2$O |
|-----------|-----------|-----------|--------|
| 1         | 11        | 88        | 1      |
| 2         | 11        | 87        | 2      |
| 3         | 11        | 86        | 3      |
| 4         | 11        | 85        | 4      |
| 5         | 11        | 83        | 6      |

3.2. Thermal behaviour

DSC curves for all studied glass compositions are presented in figure 2. The thermal behaviour slightly depends weak on the composition, there are no melting peaks on all curves. The glass transition and crystallization temperatures are summarized in table 2, one can see, that the crystallization temperature does almost not depend on composition, while the glass transition temperature slightly grows.

![DSC curves](image)

**Figure 2.** DSC curves for some 10P$_2$O$_5$–xNa$_2$O–(90-x)V$_2$O$_5$ glasses (the heating rate is 10 °C·min$^{-1}$).
Table 2. Characteristic temperatures and thermal stability range of 10P$_2$O$_5$–xNa$_2$O–(90–x)V$_2$O$_5$ glasses$^a$.

| $x$, mol. % | $T_g$, °C | $T_c$, °C | $T_c - T_g$, °C |
|-------------|-----------|-----------|-----------------|
| 0           | 226 [10]  | 267 [10]  | 41              |
| 1           | 233       | 266       | 33              |
| 2           | 234       | 266       | 32              |
| 3           | 237       | 267       | 30              |
| 4           | 238       | 268       | 30              |
| 5           | 238       | 268       | 30              |

$^a$The $T_g$ and $T_c$ values are given with error of 1 °C.

3.3. Density and molar volume

As it is seen from figure 3, molar volume of the studied glasses changes non-linearly on the Na$_2$O content and passes through the maximum at 3 mol.% Na$_2$O; the behavior of density concentration dependence is opposite. A decrease in density can be connected with the difference in densities of sodium and vanadium oxides: Na$_2$O is significantly lighter than V$_2$O$_5$. An increase in molar volume might be caused by the rearrangement of network leading to the VO$^5$ → VO$^4$ conversion, as it was reported for Li$_2$O–V$_2$O$_5$ crystalline compounds [12]. The further density growth (decreasing the molar volume) is typical for phosphate glasses (for example, [13]) and might be connected with denser package of phosphate-vanadate chains.

![Figure 3. Density and molar volume as function of Na$_2$O content in 10P$_2$O$_5$–xNa$_2$O–(90–x)V$_2$O$_5$ glasses. The first point ($x = 0$) is taken from [10].](image)

3.4. Raman spectroscopy

The influence of small additives Na$_2$O on the structure of 10P$_2$O$_5$–xNa$_2$O–(90–x) V$_2$O$_5$ glasses was studied by Raman spectroscopy (figure 4). It can be seen that in all cases, the introduction of sodium does not have a significant effect on the glass structure; only weak shifts and redistributions of the peak intensities can be noted. Since V$_2$O$_5$ concentration in the studied glasses is high, the main part of vibrations in Raman spectra is expected to belong to the vibrations of vanadium network. However, phosphorous structural groups also contribute to the network building. Therefore, in some cases it is impossible to determine which vibrations can be described by a peak. According to the literature data, peaks at ~ 145, 930, and 993 cm$^{-1}$ are attributed to the vibrations of only vanadium network: interlayer V–O bonds connecting the tops of vanadium-oxygen bipyramids [14], V–O–V and O–V–O bonds in VO$_4$ groups [15-18], and V=O bonds in VO$_3$ tetragonal pyramids [19], respectively. Peaks at 403 –
407, 530 and 706 cm⁻¹ can be connected with bending vibrations of O–P–O and O–P bonds and PO₄ groups [15, 16, 20] and symmetric stretching vibrations of P–O–P bonds [19]. The rest of peaks can be attributed to vibrations of phosphorous-oxygen at vanadium-oxygen bonds. The peak at 281-285 cm⁻¹ is connected with bending vibrations of O–P–O and V–O bonds [15, 21]. The peak at 1020 cm⁻¹ is attributed to the vibrations of V=O bonds and PO₃ groups [17, 20, 22].

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3.5. Electrical conductivity
Since Na⁺ ions can contribute to the electrical conductivity, it was measured by impedance spectroscopy (IS) and current interrupt method (CI), the combination of these methods allows electronic and ionic conductivity to be distinguished. Figure 5a presents the data obtained by two independent techniques in the Arrhenius coordinates. Good agreement of the obtained data indicates that conductivity of the studies glasses is electronic. Figure 5b demonstrates concentration dependences of conductivity logarithm (lgσ) on sodium oxide content. It is seen that the introduction of 1 mol% of Na₂O gives a sharp increase in conductivity and the further addition of Na₂O leads to the conductivity decreasing.

3.6. Simulation results
A snapshot of the final configuration of the simulated glass (x = 5 composition) is given in figure 6. One can see vanadate-phosphate chains and position of sodium ions. The typical radial distribution functions (RDF) are shown in figure 7. The first two peaks on RDF for V…O pairs (figure 7a) corresponds to double and single V–O bonds, the detailed comparison with experimental bond lengths is given in our previous work [10]. The peak position on the Na…O RDF (figure 7b) is close to 2.4 Å.
which is in excellent agreement with an array of experimental data [23]. As conductivity in such glasses is provided by electron jumps between vanadium ions, its value depends on probability of finding one vanadium ion near another one. This probability is correlated with mean coordination number (CN), which can be calculated from RDF:

\[
n_{AB}(r) = \frac{4\pi N_B}{V} \int_0^r g(r) r^2 dr,
\]

where \( n_{AB} \) is the coordination number of particle A by particles B, \( V \) is the system volume, \( N_B \) is the number of B particles, \( g(r) \) is the corresponding RDF, and \( r \) is the interatomic distance. In a range of 3.08-3.12 Å (figure 8a) an arrangement order of the CN curves is the same as for conductivity values. So, one can conclude that the maximal possible length of electron jumps between two vanadium cations light in this range. The values of the conductivity logarithm as a function of mean V…V CN is presented in figure 8b. One can see that the conductivity logarithm depends linearly on the V…V coordination number.

**Figure 6.** A snapshot of the simulated 5Na₂O·10P₂O₅·85V₂O₅ glass (a thin slice). Colors online: pentavalent V is gray, tetravalent V is blue, P is pink, double-bonded oxygen is yellow, other O types are red, Na⁺ is green.

**Figure 7.** Radial distribution functions for (a) V…O pair, (b) Na…O and Na…Na pairs and (c) V…V and V…Na pairs for the simulated 5Na₂O·10P₂O₅·85V₂O₅ glass.
4. Conclusions
Properties and structure of 10P$_2$O$_5$–xNa$_2$O–(90–x)V$_2$O$_5$ ($x = 1$–5) glasses were studied by picnometry, differential scanning calorimetry, impedance spectroscopy, current interrupt, Raman spectroscopy, as well non-constant field molecular dynamic with self-assembly. Glass transition temperature changes monotonically as Na$_2$O content increases and crystallization temperature remains the same. Density of glasses passes though the minimum at $x = 3$ mol% which might be caused by both replacement of heavy vanadium cations with light sodium ones and structural changes connected with changing the valence state of vanadium atoms. No significant changes in glass structure were observed in Ramen spectra. The conductivity in the studied glasses is provided by electron carriers; this is confirmed by the combination of AC and DC methods. The observed dependence of the conductivity on the composition is well explained by the changes in the V…V coordination number. The value of mean coordination number was obtained by computational models designed by molecular dynamics with self-assembly.

5. References
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