Critical $V_2O_5/TeO_2$ Ratio Inducing Abrupt Property Changes in Vanadium Tellurite Glasses

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ABSTRACT: Transition metal containing glasses have unique electrical properties and are therefore often used for electrochemical applications, such as in batteries. Among oxide glasses, vanadium tellurite glasses exhibit the highest electronic conductivity and thus the high potential for applications. In this work, we investigate how the dynamic and physical properties vary with composition in the vanadium tellurite system. The results show that there exists a critical $V_2O_5$ concentration of 45 mol %, above which the local structure is subjected to a drastic change with increasing $V_2O_5$, leading to abrupt changes in both hardness and liquid fragility. Electronic conductivity does not follow the expected correlation to the valence state of the vanadium as predicted by the Mott–Austin equation but shows a linear correlation to the mean distance between vanadium ions. These findings could contribute to designing optimum vanadium tellurite compositions for electrochemical devices. The work gives insight into the mechanism of electron conduction in the vanadium tellurite system.

1. INTRODUCTION

Transition metal containing oxide glasses exhibit a unique set of optical and electrical properties. 1–7 Owing to their high electronic conductivity, they have often been applied in electrochemical devices. 8–13 In particular, vanadium tellurite glasses show higher electronic conductivity than other vanadium containing oxide glasses such as phosphates, borates, and silicates 14–21 and therefore have attracted much attention of scientists. 3–9,11–13 4 The compositional dependence of hardness in the $TeO_2$–$V_2O_5$ glass system has been studied to some extent. 12,23 The structure of this glass system has been determined using nuclear magnetic resonance spectroscopy, neutron and X-ray diffraction, and Raman spectroscopy. 24–26 In the vanadium tellurite system, the effect of the composition on glass transition temperature ($T_g$) has been explored, 3,27,28 and the liquid fragility index ($m$), i.e., the speed of the viscosity change at $T_g$ upon cooling or heating, has been determined. 3,4 More recently, the electronic conductivity of $2TeO_2$–$V_2O_5$ glass ceramics was studied as a function of the degree of crystallinity. 29 To the best of our knowledge, a systematic study has not been reported concerning the compositional dependence of both static and dynamic properties of vanadium tellurite glasses. In order to better understand the composition–structure–property relationship of this glass system and thereby tailor its electrochemical performance, it is necessary to perform a thorough study of the dynamic, electrical, and physical properties. Another interesting aspect of this study is to verify whether the vanadium tellurite liquids are indeed so fragile as reported in previous studies. 3,4,29 If this is the case, we should explore the structural origin of the high fragility of these glass liquids.

In this study, we determine the valence state ratio of vanadium ($\epsilon$), $m$, $T_g$, Vickers hardness ($H_v$), density ($\rho$), electronic conductivity ($\sigma$), and glass stability via the Hruška parameter ($K_n$) of vanadium tellurite glasses. We focus on the compositional dependences of these properties and explain their structural origin. The knowledge gained from this work could be used for designing vanadium tellurite glass compositions for electrochemical devices.

2. EXPERIMENTAL SECTION

Glass samples were prepared via the melt quenching technique, using reagent grades of $\geq 99.6$% $V_2O_5$ and $\geq 99.5$% $TeO_2$. A series of $V_2O_5$–$TeO_2$ glasses with various $V_2O_5$ contents were synthesized by mixing and milling the batches of both oxide materials for 0.25 h, melting them at 800 °C for 0.5 h, quenching the melt on a brass plate, and finally annealing the formed glasses for 2 h at their respective $T_g$. The amorphous state of all glasses was verified by X-ray diffraction (Rigaku, Ultima IV) using Cu Kα radiation, and their final chemical compositions were determined by energy dispersive X-ray spectroscopy (Phenom). The analyzed chemical compositions are given in Table 1. Compositions are described by the molar percentage of vanadia, namely, $X = [V_2O_5] / ([V_2O_5] + $
Table 1. Chemical Composition of the Six Vanadium Tellurite Glasses with Various V$_2$O$_5$ Contents$^a$

<table>
<thead>
<tr>
<th>sample name</th>
<th>V$_2$O$_5$ [mol %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>VT_10</td>
<td>9.7</td>
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<tr>
<td>VT_20</td>
<td>19.9</td>
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<td>VT_30</td>
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<td>VT_50</td>
<td>50.2</td>
</tr>
<tr>
<td>VT_65</td>
<td>65.8</td>
</tr>
</tbody>
</table>

$^a$The compositions were analyzed by energy dispersive X-ray spectroscopy (±0.3 mol %).

*[TeO$_2$]). Room-temperature density was determined by gas pycnometry (Quantachrome, Ultrapyc 1200e) using helium as pressure gas.

Coplanar samples of each composition were polished and sputtered with gold before electronic conductivity was measured by impedance spectroscopy (Solartron, SI1260). The electrical measurements were performed in air with a two-point sample holder from 303 to 523 K and with an applied voltage of 100 mV in the frequency range from $10^6$ to 1 Hz. Impedance data were plotted in an impedance complex plane (Nyquist diagram) and fitted by an equivalent circuit consisting of one resistor in parallel with one capacitor. The dc resistances ($R_s$) were thus determined by the intercept of the semicircle to the real axis at low frequency. $\sigma$ was calculated as $\sigma = (1/R_s) (I/S)$ ($I$ and $S$ are the thickness and the surface area of the sample in contact with the electrode, respectively). $H_v$ was measured via a Knoop pyramid indenter (Duramin, Struers). A total of 30 indents were made on each sample using an indentation time of 10 s and an indentation load of 0.25 N. The measurements were performed in air at room temperature.

The liquid fragility indices were determined by a linear fitting of the viscosity data around $T_g$. The viscosities in the range of $\eta = 10^{11}$–$10^{13}$ Pa s were measured using a ball penetration viscometer (Bähr, Vis 405). For each data point, a minimum of five penetrations were made at a specific temperature. The pressing ball was made of silica. Press depth was 300 $\mu$m, and the press load was between 2 to 9 N.

Calorimetric measurements were performed on a differential scanning calorimeter (DSC) (Jupiter 449C, Netzsch) in order to determine the calorimetric glass transition temperature ($T_g$), the crystallization onset temperature ($T_c$), the melting onset temperature ($T_m$), and the isobaric heat capacity jump during the glass transition ($\Delta C_p$). Each sample was initially subjected to an upscan to 700 $^\circ$C at 10 K/min in order to determine $T_c$ and $T_m$. Subsequently each composition is subjected to a downscan and an upscan at 10 K/min to approximately 100 K above $T_g$. The first upscan curves reflect the thermal history of an unknown cooling rate, whereas the second upscan curves reflects the standard thermal history of a cooling of 10 K/min during the first downscan. A flow of 40 mL/min argon was used as protective gas, and gold crucibles were used for both sample and reference. Both $T_g$ and $\Delta C_p$ were determined from the second upscan. In order to calculate the isobaric heat capacity ($C_p$) of the vanadium tellurite glasses, a 63 mg sapphire standard was utilized.

The concentration of $V^{4+}$ was determined by electron paramagnetic resonance (EPR) spectroscopy. For each sample approximately 20 mg of powder was measured at room temperature in a Bruker EMX X-band EPR spectrometer with an ER 4102ST cavity and a Gunn-diode microwave bridge. The spectra were obtained from 2850 to 3500 G at microwave frequency 9.58 GHz, microwave power 6.31 mW, modulation frequency 100 kHz, and modulation width 8 G and were accumulated over 10 sweeps. Identical settings were used for five standards containing known concentrations of VO(SO$_4$)$_2$·3H$_2$O (Sigma-Aldrich) in K$_2$SO$_4$ (Sigma-Aldrich).

3. RESULTS

Figure 1 shows the first DSC upscans of the vanadium tellurite glasses. $T_c$ is defined as the crystallization onset temperature, whereas $T_m$ is determined as the onset temperature of the melting peak. Figure 2 demonstrates the nonlinear dependence of $T_g$ on the V$_2$O$_5$ content of the vanadium tellurite glasses. The inset illustrates how to determine the characteristic calorimetric temperatures ($T_g$, $T_c$, and $T_m$) as a function of content $X$. $T_g$ is a measure of the thermodynamic liquid fragility.

$$C_p = \frac{C_{pl} - C_{pg}}{X}$

whereas $T_m$ is determined as the onset temperature of the melting peak.

Figure 2. Glass transition temperature ($T_g$) as a function of $X$ ([V$_2$O$_5$]/([V$_2$O$_5$] + [TeO$_2$])) of the vanadium tellurite glasses. The solid line is a guide for the eye showing the compositional scaling of $T_g$. Inset: Determination of the $C_p$ jump during the glass transition, i.e., $\Delta C_p = C_{pl} - C_{pg}$, taking the 30 mol % V$_2$O$_5$ glass as an example. The error range of the $T_g$ values is ±2–3 K.

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The dependence of \( K_H \) on \( X \) obeys a Gaussian distribution with a maximum very close to the congruent composition of \( \text{V}_2\text{O}_5-2\text{TeO}_2 \). In Figure 4 \( c = \left[ \text{V}^{4+} \right] / \left[ \text{V}_{\text{total}} \right] \) is plotted as a function of \( X \) (\( \left[ \text{V}_{\text{total}} \right] \) is the total amount of vanadium ions, i.e., equal to \( \left[ \text{V}^{4+} \right] + \left[ \text{V}^{5+} \right] \)). Initially as \( X \) increases, \( \left[ \text{V}^{4+} \right] / \left[ \text{V}_{\text{total}} \right] \) remains constant at around 5%. At \( X = 0.45 \) an abrupt change in slope occurs, and the \( \left[ \text{V}^{4+} \right] / \left[ \text{V}_{\text{total}} \right] \) ratio drastically decreases with further increase in \( X \). \( \left[ \text{V}^{4+} \right] / \left[ \text{V}_{\text{total}} \right] \) is defined as \( c \) in the Mott–Austin equation (eq 3).

Liquid fragility index \( (m) \) of the glass systems is determined by a linear fit of the viscosity data around \( T_g \) (see inset of Figure 5), i.e., through the following relation:

\[
 m = \frac{\partial \log \eta(T)}{\partial (T_g/T)} 
\]

The dependence of \( m \) on \( X \) is illustrated in Figure 5. \( m \) remains unchanged at \( \sim 80 \) for \( X \) between 0.1 and 0.45 but drastically increases linearly up to \( m = 105 \) when \( X \) increases from 0.45 to 0.65. Supposing that this trend continues, vitreous \( \text{V}_2\text{O}_5 \) would have an \( m \) value of 147.

Since \( H_v \) strongly depends on the condition of indentation, all microindentation experiments were performed with the same indentation load and time (0.25 N and 10 s), ensuring crack free indents. The \( H_v \) values are plotted in Figure 6 as a function of \( X \). \( H_v \) remains constant when \( X \) increases from 0.1 to 0.45, followed by a linear decrease with further increasing \( X \) from 0.45 to 0.65. Considering the experimental error associated with the hardness determinations, the compositional hardness scaling agrees with that reported in

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**Table 2. Glass Transition Temperature (\( T_g \)), Crystallization Onset Temperature (\( T_c \)), Melting Onset Temperature (\( T_m \)), Glass Stability Parameter (\( K_H \)), and Heat Capacity Jump at \( T_g \) (\( \Delta C_p \)) Obtained from Differential Scanning Calorimetry**

<table>
<thead>
<tr>
<th>sample name</th>
<th>( T_g ) [K]</th>
<th>( T_c ) [K]</th>
<th>( T_m ) [K]</th>
<th>( K_H ) [-]</th>
<th>( \Delta C_p ) [J mol(^{-1}) K(^{-1})]</th>
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<tr>
<td>VT_10</td>
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<td>679</td>
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<td>704</td>
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<td>682</td>
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<td>743</td>
<td>0.4</td>
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</tr>
<tr>
<td>VT_65</td>
<td>500</td>
<td>531</td>
<td>746</td>
<td>0.1</td>
<td>191.6</td>
</tr>
</tbody>
</table>
literature, viz., a decrease in \( H_g \) with increasing \( X \). The compositional behavior of \( H_g \) (Figure 6) resembles that of \( c \) (Figure 4), i.e., an initial plateau followed by a decrease with further increase in \( X \).

Room temperature density and molar volume \( (V_m) \) are presented in Figure 7. \( V_m \) is calculated as the molar mass divided by the glass density. Density exhibits a linear decrease with increasing \( X \), whereas the molar volume increases nonlinearly.

Electronic conductivity of glasses containing transition metal oxide is evaluated via the Mott–Austin equation (eq 3),

\[
\sigma = \frac{\log^2 \nu_e}{Rk_B T} \left( 1 - c \right) e^{-2\alpha R} e^{-W/(k_B T)}
\]

where \( \nu_e \) is the optical phonon frequency, \( R \) is the mean distance between the ions where the electron transfer occurs (vanadium ions in this case), \( \alpha \) is the tunneling factor, and \( W \) is the activation energy. The parameters of the Mott–Austin equation can be determined by plotting \( \log(\sigma T) \) vs 1000/\( T \) and fitting eq 3 to each set of conductivity data. This is performed in Figure 8, and the derived parameters are shown in Table 3. In order only to have two fitting parameters (namely, \( \alpha \) and \( \nu_e \)), \( c \) and \( R \) are determined by EPR and pycnometry, respectively. \( R \) is calculated as per eq 4,

\[
R = \left( \frac{M_W}{2M \rho N_A} \right)^{1/3}
\]

where \( M_W \) is the molar mass, \( M \) the molar concentration of conductive sites (i.e., vanadium), \( \rho \) the density, and \( N_A \) Avogadro’s constant. \( R \) is plotted in the inset of Figure 9 and \( c \) values are plotted in Figure 4. In Figure 8 it is seen that the electronic conductivity of the vanadium tellurite glasses increases with \( X \). The observed increase in electronic conductivity with increasing \( V_2O_5 \) is in good agreement with that reported elsewhere. In order to better visualize this correlation, electronic conductivity data at 298 K \( (\sigma_{298K}) \), along with \( W \), are plotted in Figure 9 as a function of \( X \). The \( \log(\sigma_{298K}) \) initially increases with \( X \), while \( W \) decreases. Both quantities reach a plateau when \( X \) surpasses the critical value of about 0.45.

4. DISCUSSION

The decrease in \( \rho \) with increasing \( X \) (Figure 7) indicates a looser packing of the atoms, since the molar mass of \( V_2O_5 \) is higher than that of \( TeO_2 \). The observed increase in \( V_m \) implies that \( V_2O_5 \) constitutes a less compact structural arrangement. The structural expansion with increasing \( X \) causes a decrease in the bond numbers per unit volume, i.e., a decrease of constraints, and hence a decrease in \( T_g \) (Figure 2 and Table 2). The decrease of \( \rho \) and \( T_g \) with increasing \( X \) has also been reported in previous studies, e.g., \( T_g \) drops from 560 to 505 K when \( V_2O_5 \) is raised from 10 to 50 mol %.

In contrast, the onset temperature of crystallization \( (T_c) \) first decreases with \( X \) and then increases (Table 2). The melting temperature \( (T_m) \) only slightly varies in an irregular manner. Consequently, according to eq 1, the glass stability parameter \( (K_{gt}) \) first increases and then decreases with increasing \( X \). The trend manifests itself as a Gaussian distribution of \( K_{gt} \) over \( X \) with a maximum around \( X = 0.3 \) (Table 2). This is consistent with a previous study, but different from another study, where the glass stability is found to linearly increase with increasing \( X \).

Vanadium tellurite glasses have been reported to contain both \( VO_4 \) and \( VO_5 \) polyhedra, where \( V^{4+} \) primarily exists in tetragonally distorted octahedral coordination, and \( V^{5+} \) mainly exists in a trigonal bipyramidal configurational (~80%) at low \( V_2O_5 \) concentrations. As the \( V_2O_5 \) concentration increases, the energetically preferred coordination geometry of \( V^{5+} \) however changes from a trigonal bipyramidal coordination at low \( V_2O_5 \) concentrations to a 50/50 mixture of trigonal bipyramidal and tetrahedral configuration at high \( V_2O_5 \) concentrations. By comparison of \( \rho \) and \( c \) obtained in this work with the structural environment of vanadium in vanadium tellurite glass obtained in literature, an increase in tetrahedral sites could cause an expansion of the glass network (Figure 7) and consequently decrease the amount of bonds per unit volume (decrease in connectivity and \( T_g \); see Figure 2). If all \( V^{4+} \) ions are assumed to occupy tetragonally distorted octahedral sites, from Figure 4 we can infer that the fraction of distorted tetrahedral sites starts to drop at \( X = 0.45 \).

At a certain \( c \) value, the \( V^{4+} \) ions start to contribute more constraints to the network than \( V^{5+} \), leading to the onset of both the increase in \( m \) (Figure 5) and the drop in \( H_g \) (Figure 6) at about \( X = 0.45 \). When the fraction of tetragonal \( V^{4+} \) sites...
starts to decrease, the quantity of the most constrained network diminishes, leading to a decrease in \( H_\alpha \) and an increase in \( m \). Sharma et al.\(^{23}\) measured \( H_\alpha \) and \( \epsilon \) of vanadium phosphate, vanadium tellurite, and vanadium borate glasses and found that in these systems the \( \epsilon \) value decreases with an increase in \( X \), almost parallel to a 1:1 decrease in \( H_\alpha \). As demonstrated in Figures 5 and 6, the ratio of \( V^{4+} \) to total vanadium is seen to have significant impact on both \( H_\alpha \) and \( m \). According to Figures 4–6 and a previous work,\(^{23}\) \( \epsilon \) is believed to impact the physical and dynamic properties of the studied glass, since it affects the structure of these glasses. For the three different vanadium systems, an approximate 1:1 correlation is found between \( H_\alpha \), \( m \), and \( \epsilon \).

A change in \( \epsilon \) affects the local structural arrangements in the studied glasses and hence results in a mismatch in constraints between the two involved structural arrangements (i.e., \( V^{4+} \) in tetragonally distorted octahedral coordination and \( V^{5+} \) in a trigonal bipyramidal coordination). As both \( H_\alpha \) and \( m \) have been shown to linearly depend on the total amount of constraints in the network,\(^{47,48}\) a direct link might occur between \( H_\alpha \), \( m \), and \( \epsilon \). \( H_\alpha \) and \( m \) are measured at different temperatures, but the structural arrangements that \( \epsilon \) differentiates between might exhibit a constraint mismatch both at room temperature and at \( T_g \). The \( m \) value of the vanadium tellurite glass with 40 mol % \( V_2O_3 \) was found by Souri to be 70.\(^{4} \) This \( m \) value is only slightly lower than that shown in Figure 5 considering the relatively large error range of \( m \).

Consistent with the change of the kinetic fragility (\( m \)), the \( C_p \) jump across the glass transition (\( \Delta C_p \)) (see Table 2) also increases with increasing \( X \). \( \Delta C_p \) is a measure of the thermodynamic fragility. This implies that the change of the configurational entropy during the glass transition is associated with that of the valence state of the vanadium. This means that the change of the local structural environment scales with the change in the configurational entropy.

In contrast, electronic conductivity does not show the same compositional trend as \( H_\alpha \) and \( m \), indicating that other structural factors rather than \( \epsilon \) dictates the electronic conductivity. As shown in Figure 9, the electronic conductivity measured at 298 K (log(\( \sigma_{298K} \))) initially increases with \( X \) and then remains almost unchanged above \( X = 0.45 \), exactly where \( \epsilon \) drastically drops. This is surprising, as eq 3 predicts an increase in log(\( \sigma_{298K} \)) with increasing \( \epsilon \) (for \( \epsilon < 0.5 \)). The compositional scaling of log(\( \sigma_{298K} \)) matches that of the mean distance between vanadium ions (\( R \)) (see inset of Figure 9), since eq 3 predicts \( R \) and log(\( \sigma_{298K} \)) to be inversely proportional. The exact same trend is observed for \( W \) (Figure 9), and the linear relation between \( W \) and \( R \) is well documented for vanadium tellurite glasses.\(^{7,9,49,50}\) On the basis of Figures 8 and 9, we can infer that the electronic conductivity of the vanadium tellurite glasses depends linearly on \( R \). This is not surprising, as the electron hopping is strictly adiabatic, as exp\((-2aR) = 1 \) for all compositions (see Table 3). In the adiabatic case we expect a linear influence of \( R \) on \( \sigma \). The fact that electron hopping occurs adiabatically in vanadium tellurite glass is in good agreement with former measurements.\(^{44,51,52}\) In order to achieve higher conductivity, the vanadium ions must thus be brought closer to each other, i.e., an increase in density. This implies that the electronic conductivity is not so dependent on \( \epsilon \) as predicted by the Mott–Austin equation (eq 3). When \( \epsilon \) varies, \( VO_3 \) and \( VO_2 \) polyhedra are interchanging, leading to changes in \( R \). It might be this change in \( R \) that facilitates the changes in log(\( \sigma_{298K} \)).\(^{9,11,19–21,49,50}\) For an electrochemical application, e.g., cathode materials in secondary lithium batteries, it is important to optimize the relevant properties such as \( m \), \( H_\alpha \), and \( \sigma \) of the vanadium tellurite glass. This work contributes to establishing the knowledge basis for designing battery materials. Certainly, further studies still need to be done in order to clarify the detailed microscopic mechanism of the abrupt change of the studied properties at the critical \( V_2O_3 \) concentration. In particular, a detailed structure analysis by small angle neutron/X-ray diffraction techniques and molecular dynamic modeling will provide additional information on the role of the structure in determining the properties of the vanadium tellurite glass systems.\(^{53,54}\)
5. CONCLUSION

We have observed a critical $V_2O_5$ concentration in the vanadium tellurite glasses, above which the local structure undergoes a drastic change, leading to an abrupt change in both physical and dynamic properties.

Hardness and liquid fragility of the studied glasses remain almost unchanged with $X$ when $X < 0.45$. However, when $X$ exceeds 0.45, hardness drops whereas the liquid fragility rises. This means that there is a critical $V_2O_5$ concentration of $X = 0.45$, above which an abrupt change of the glass properties takes place. The observed trends in hardness and liquid fragility are closely related to the valence ratio of the vanadium ions ($c$), as $c$ shows the same trend. The reason for this coincidence could be that $V^{2+}$ results in a more constrained structure than $V^{3+}$, i.e., in fewer constraints per unit volume and hence in lower hardness and higher fragility.

The electronic conduction of vanadium tellurite glasses occurs strictly adiabatically, and $\sigma$ does not follow the expected correlation to $c$ as predicted by the Mott—Austin equation; instead it exhibits a linear correlation to $R$. If the decoupling of $\sigma$ from $c$ also occurs at higher $c$ values, it enables optimization of hardness and liquid fragility without influencing $\sigma$.

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The authors declare no competing financial interest.

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REFERENCES


