

IONIC AND ELECTRONIC CONDUCTIVITY OF GLASSES IN THE P₂O₅-V₂O₅-Na₂O SYSTEM

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The conductivity of glasses in the y P₂O₅ - $(1-y)$ [(1-x) V₂O₅ - x Na₂O] system is studied as a function of temperature and composition. For all compositions, the conductivity variations as a function of temperature follow an Arrhenius type relationship. The activation energy and pre-exponential factor values determined for the V₂O₅ richest compositions are lower than those obtained for the rich ionic domain. Isothermal variations of the conductivity as a function of composition show deep minima for molar ratios x near 0.65. On either side of these minima, the conductivity is mainly electronic ($x < 0.6$) or ionic ($x > 0.8$). The variations are interpreted assuming a prevailing diluting effect of the non predominantly present oxide with no interactions between the electronic and ionic charge carriers.

INTRODUCTION

Oxide based glasses, containing V₂O₅ as active component have been selected to be used as cathode material in alkali anodes batteries. During the discharge process, an alkali atom is inserted in the glassy disordered structure under a ionic form and the remaining electron reduces the vanadium from the +V to the +IV valence state. The intercalation and reduction processes could occur only if the material simultaneously exhibits a mixed conductivity, i.e. both ionic and electronic. In glassy systems, the two types of conductivity are low. Moreover, it has been recently pointed out that the electronic and ionic charge carriers may interfere, leading to significant decreases of each conductivity. This phenomenon has been compared to the so called mixed alkali effect [1]. To clarify that point, we have undertaken a systematic study of the electrical behaviour of glasses in the P₂O₅-V₂O₅-Na₂O ternary system. Samples have been prepared by keeping constant the molar ratio of the network former (P₂O₅) while progressively substituting the "electronically active" oxide (V₂O₅) by the "ionically active" network modifier (Na₂O).

Results obtained on the 0.5 P₂O₅ - 0.5 [(1-x)V₂O₅ - x Na₂O] system have been presented in a previous paper [2]. To establish the influence of the network former concentration on the glasses electrical properties, two new sets of compositions have been synthesised and characterised.

EXPERIMENTAL PART

Glass preparation

All glasses were prepared under atmospheric conditions by heating appropriate quantities of (NH₄)H₂PO₄ (Merck 99 %), Na₂CO₃ (Prolabo RP 99,8 %) and V₂O₅ (Merck RP) previously dried at 80 °C. The mixtures, stirred to remove CO₂, were melted for one hour in a rhodium-platinum crucible at temperatures ranging from 800 °C to 1100 °C. The highest melting temperatures were required for vanadium rich glasses. At high temperature, the following redox equilibrium takes place:



leading to concentrations of the oxidised and reduced forms of same order of magnitude [3]. The melts were quenched in air by pouring them in an aluminium mould at room temperature and then annealed for one hour at roughly 20 °C below the glass transition temperature, T_g . Three sets of compositions (a, b and c) with a constant molar ratio in P₂O₅ were prepared which are represented as dots in the ternary diagram of the system shown in figure 1.

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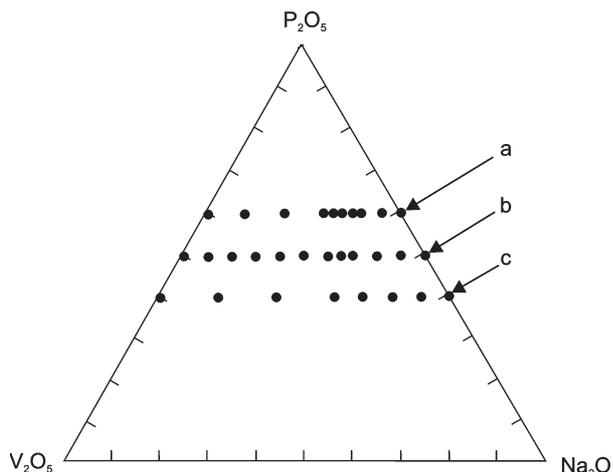


Figure 1. The actual synthesised compositions ($a : y = 0.6$, $b : y = 0.5$, $c : y = 0.4$) of the P_2O_5 - V_2O_5 - Na_2O system.

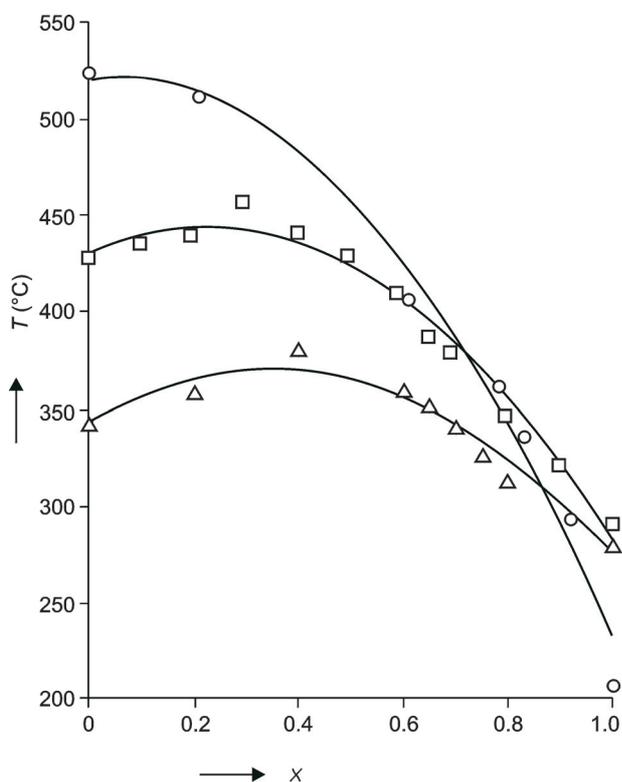


Figure 2. Variations of the glass transition temperature, T_g , with substitution ratio, x ($x = Na_2O / (Na_2O + V_2O_5)$), for the $y P_2O_5 - (1-y) [(1-x) V_2O_5 - x Na_2O]$ glass systems.
 $\circ - y = 0.6$, $\square - y = 0.5$, $\triangle - y = 0.4$

The samples follow the general formula $y P_2O_5 - (1-y) [(1-x) V_2O_5 - x Na_2O]$ with $y = 0.4, 0.5, 0.6$ and $0 \leq x \leq 1$. The samples composition was checked by chemical analysis (flame spectroscopy) of sodium, phosphorous and vanadium and a difference of less than

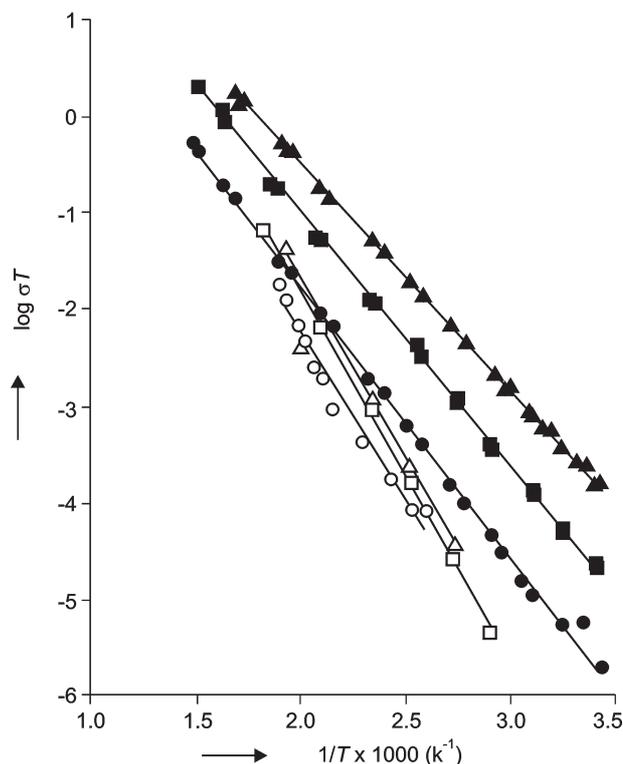


Figure 3. Arrhenius plot of the conductivity for vanadium rich ($x = 0.2$) and sodium rich ($x = 0.9$) samples.

$\bullet - x = 0.2, y = 0.6$; $\blacksquare - x = 0.2, y = 0.5$; $\blacktriangle - x = 0.2, y = 0.4$;
 $\circ - x = 0.9, y = 0.6$; $\square - x = 0.9, y = 0.5$; $\triangle - x = 0.9, y = 0.4$

1 % was found between expected and actual compositions.

The colour of the glasses ranged from black to light yellow when the Na_2O molar concentration is gradually increased from $x = 0$ to $x = 1$. The vitreous nature of the samples was confirmed by X-rays spectrographs.

The glass transition temperatures, T_g , were determined using DTA (Netzsch ST 409) with a standard heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. These temperatures range from $520 \text{ }^\circ\text{C}$ down to $200 \text{ }^\circ\text{C}$ as shown in figure 2. For each set of P_2O_5 compositions, the highest transition temperatures were determined for glasses mainly containing vanadium oxides ($0 \leq x \leq 0.5$) whereas they strongly decrease for sodium rich samples ($0.5 \leq x \leq 1$). This behaviour can be related to the fact that V_2O_5 is a conditional glass former while Na_2O is a glass modifier. It should be mentioned that glasses with large Na_2O content ($x < 0.8$) tend to easily crystallise over their glass transition temperature.

RESULTS

Conductivity measurements

For conductivity measurements, glass pellets of 12 mm in diameter and about 1 mm thick, are directly shaped in the mould during the cooling stage and no

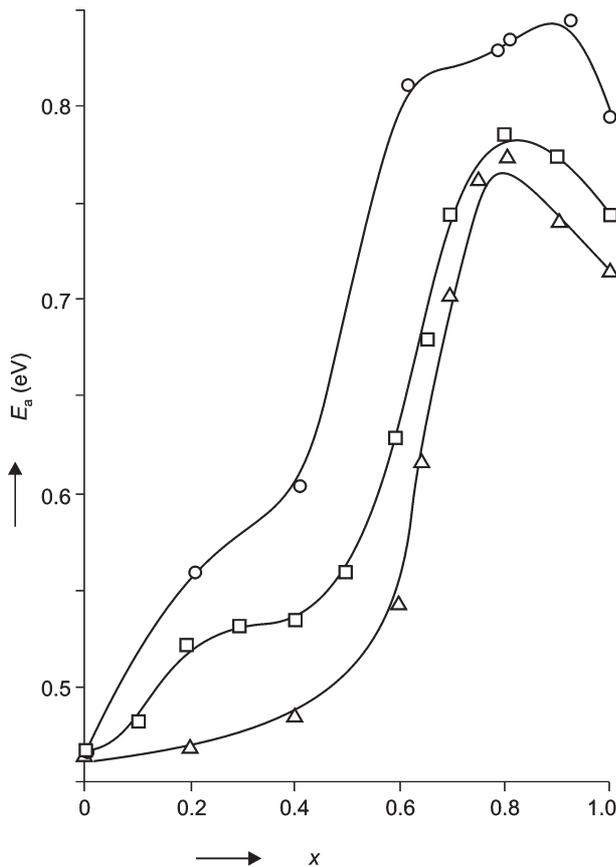


Figure 4. Variations of the activation energy, E_a , with substitution ratio, x , ($x = Na_2O/(Na_2O+V_2O_5)$), for the $y P_2O_5 - (1-y) [(1-x) V_2O_5 - x Na_2O]$ glass systems.
 ○ - $y = 0.6$, □ - $y = 0.5$, △ - $y = 0.4$

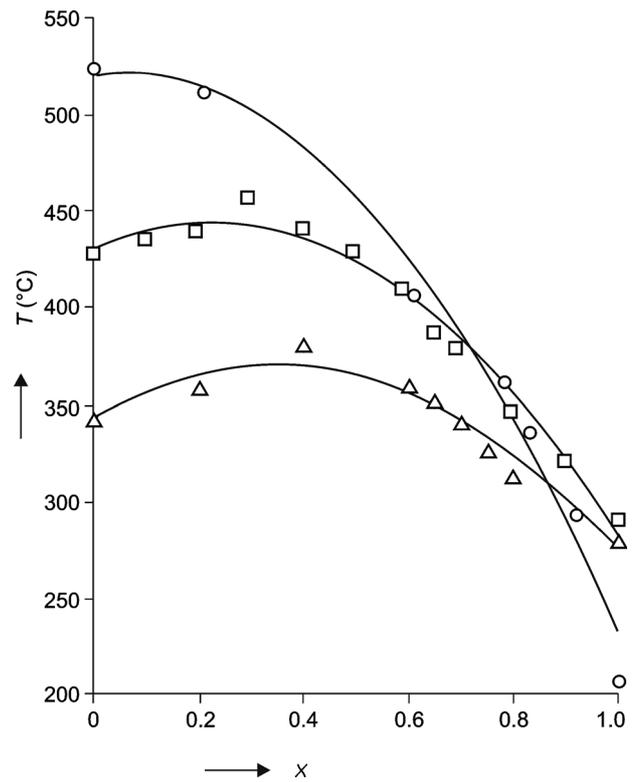


Figure 5. Variations of the pre-exponential factor, A , with substitution ratio, x , ($x = Na_2O/(Na_2O + V_2O_5)$), for the $y P_2O_5 - (1-y) [(1-x) V_2O_5 - x Na_2O]$ glass systems.
 ○ - $y = 0.6$, □ - $y = 0.5$, △ - $y = 0.4$

additional machining is required. In order to realise the electrodes, the two flat surfaces of the glass pellets were painted with a solution of colloidal graphite in isopropanol (DAG 154 Achenson). The conductivities were deduced from complex impedance measurements in the 5 Hz -13 MHz frequency range, using a Hewlett Packard 4912A impedance analyser. Impedance measurements were first carried out during a heating stage from 25 °C to about 20 °C below the glass transition temperature and then during a cooling stage.

When sodium rich glasses are heated over their glass transition temperature, a partial crystallisation may occur leading to a significant decrease in conductivity. Each measurement was made in a steady state after 20 °C to 40 °C temperature increments or decrements. No significant deviations were observed between results obtained during the two stages. For all samples, the high frequencies ($10^7 \text{ Hz} > f > 10^3 \text{ Hz}$) impedance data are represented in the complex plane by a single semicircle, confirming that they are homogeneous and single-phased. For high vanadium oxide content ($0 \leq x \leq 0.6$), impedance plots in the whole frequency range consist in only one semicircle.

For high sodium oxide content ($0.7 \leq x \leq 1$), these diagrams show the same high frequencies semi-circle, followed by a straight line at low frequencies ($f < 10^3 \text{ Hz}$), characteristic of an interfacial impedance.

Figure 3 represents the Arrhenius plot of the conductivity variations ($\sigma \times T$ product) as a function of the reciprocal temperature for two series of samples. Each series corresponds to samples containing the same amount of sodium oxide ($x = 0.2$ for the first one and $x = 0.9$ for the second one) with three different P_2O_5 contents, respectively $y = 0.4, 0.5$, and 0.6 .

For the samples which contain a large quantity of sodium oxide ($x = 0.9$), the logarithmic variations of the conductivity are linear with $1/T$ with nearly the same slope. The same behaviour is observed with the vanadium rich samples ($x = 0.2$), but the corresponding slope is less important than that of the first series. These results suggest two different conductivity mechanisms, either predominantly ionic or predominantly electronic according to the composition.

Independently on the composition, the general temperature-conductivity relationship may be expressed by the following equation:

$$\sigma \times T = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

As it may be seen in figure 4 and 5, respectively representing the variations of the activation energy, E_a , and of the pre-exponential factor, A , as a function of the substitution ratio, x , a drastic change in the evolution of the parameters appears for $0.6 < x < 0.8$, confirming the discrimination between vanadium and sodium containing glasses.

For $x \leq 0.6$, the activation energy lies around 0.5 eV and the pre-exponential term A remains around $10^4 \text{ S cm}^{-1} \text{ K}$. On the other side of the composition range, the activation energy remains close to 0.75 eV and A is close to $10^6 \text{ S cm}^{-1} \text{ K}$. In the intermediate region, isothermal variations of the conductivity, as shown in figure 6 at 400 K passes through a minimum which value is about one to two orders of magnitude lower than those of the limiting compositions ($x = 0$ or $x = 1$).

DISCUSSION

Glasses containing vanadium oxides are known to have an electronic conductivity due to a tunnelling transfer of electrons from a V^{+IV} , donor level to a V^{+V} , acceptor level. The probability of this transfer is maximal when both the donor and acceptor atoms have the same energy level. This may occur under the action of thermal vibrations of the oxygen ligands. This mechanism is known as a phonon-assisted polaron hopping process [4] and leads to the following expression of the electronic conductivity:

$$\sigma = \frac{F^2 l^2 \nu_p}{6RT} c_V y(1-y) \exp(-2\alpha l) \exp\left(-\frac{W}{RT}\right) \quad (3)$$

where ν_p is the longitudinal optical phonon frequency, C_V is the molar concentration of vanadium atoms, y is the ratio of the number of sites at the lowest valence (V^{+IV}) to the total number of vanadium ions, l is the average separation between a donor and acceptor level and W is the energy required for this hopping mechanism. The $\exp(-2\alpha l)$ term describes the overlap of the external atomic orbitals radial contribution of the vanadium atoms. In this last expression, α represents the inverse localisation length of the s-like wave function describing the localised state at each site. The above equation can be simplified as:

$$\sigma \times T = A_{\text{elec}} \exp\left(-\frac{W}{RT}\right) \quad (4)$$

where A_{elec} , denoting the pre-exponential term of the electronic conductivity, is expressed by:

$$A_{\text{elec}} = \frac{F^2 l^2 \nu_p}{6R} c_V y(1-y) \exp(-2\alpha l) \quad (5)$$

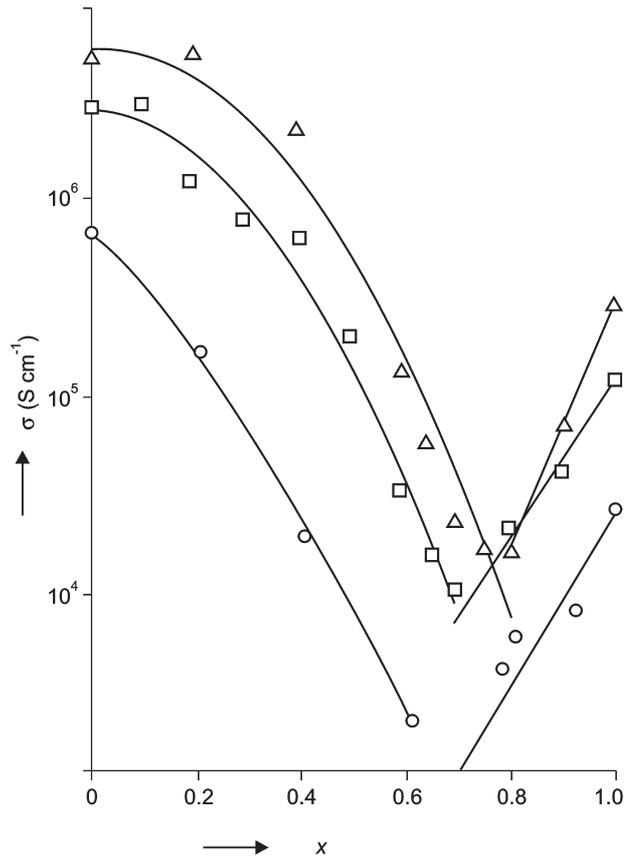


Figure 6: Variations of the conductivity at 400 K with substitution ratio, x , ($x = \text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{V}_2\text{O}_5)$), for the $y \text{ P}_2\text{O}_5 - (1-y) [(1-x) \text{V}_2\text{O}_5 - x \text{Na}_2\text{O}]$ glass systems.
 $\circ - y = 0.6, \square - y = 0.5, \triangle - y = 0.4$

The conductivity of alkali containing glasses is ionic and is essentially due to the displacement of the alkali cations. This ionic conductivity mechanism may be described in terms of ionic defects movement as it is the case in ionic crystals [5]. The suggested mechanism, i.e. an indirect interstitial mechanism leads to the expression of the ionic conductivity :

$$\sigma_i = \frac{F^2 l^2 \nu_p}{6RT} \exp\left(-\frac{\Delta G_m + \frac{\Delta G_f}{2}}{RT}\right) \quad (6)$$

In this expression, l is the mean distance between two normal sites, ν_0 is the attempt frequency, C_{Na} is the total concentration in Na^+ cations by unit volume. ΔH_f and ΔH_m are respectively the enthalpy of formation of the interstitial pair and the enthalpy of migration of this defect.

This expression can be identified to the experimental Arrhenius relationship(2), hence leading to an explicit formulation of the activation energy :

$$E_c = \Delta H_m \frac{\Delta H_f}{2} \quad (7)$$

and, neglecting the entropy terms, to that of the pre-exponential factor :

$$A_{ion} = \frac{F^2 \rho C_{Na} v_0}{6R} \quad (8)$$

These two models, either for the electronic or for the ionic conductivity, justify the Arrhenius behaviour experimentally found for the conductivity dependence on temperature.

Usually, electronic conducting glasses are characterised by lower values of both activation energy and pre-exponential factor than those obtained for ionic conducting glasses. The tunnelling electronic transfer requires less energy than that necessary for an ion to migrate. The lower values of the electronic pre-exponential term can be mainly attributed to contribution of the overlapping term, all other terms having comparable values [2]. In figure 4 and figure 5, our experimental data clearly evidence that an electronic conductivity predominates for $x \leq 0.4$ while an ionic one operates for $x \geq 0.8$.

For the three studied systems, the isothermal variations of the conductivity goes through a minimum for a value of the substitution ratio, x , which increases with increasing network former content (P_2O_5). For V_2O_5 rich glasses, the predominant electronic conductivity decreases due to the lessening of the V_2O_5 active constituent. This lowering of the conductivity may probably result from an exponential decrease in the overlapping term, which appears in the pre-exponential factor, subsequent to an increase of the mean distance between a donor and an acceptor vanadium atom. Such behaviour is well known in binary V_2O_5 -networks formers systems [6, 7].

For Na_2O rich glasses, the ionic conductivity also strongly decreases with decreasing Na_2O content. This behaviour is generally interpreted as resulting from a significant drop of the thermodynamic activity of the network modifier leading to an important diminution of the ionic charge carriers concentration. In that case, the conductivity is expected to exponentially decrease with decreasing Na_2O molar ratio [8].

CONCLUSION

According to these considerations, the existence of minima for the conductivity in the three studied systems may simply result from a dilution effect, by Na_2O in the electronic predominant region, and by V_2O_5 in the ionic predominant one. There is no need to postulate some specific interactions between both types of charge carriers as it is usually done to interpret the minimum encountered in ionic conducting glasses when one alkali is gradually substituted for another. This phenomenon, known as the "mixed alkali effect" is expressed by

sharp drops of the conductivity near the limits and accompanied by the existence of maximums for the activation energy and for the pre-exponential factor [9, 10]. This is not the case for our results which present something like a "discontinuity" of the variations of the activation energy E_a and pre-exponential term, A .

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IONTOVÁ A ELEKTRONOVÁ VODIVOST SKEL SYSTÉMU $P_2O_5 - V_2O_5 - Na_2O$

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Byla studována vodivost skel systému the $y P_2O_5 - (1-y) [(1-x) V_2O_5 - x Na_2O]$ v závislosti na teplotě a složení. Teplotní závislosti vodivosti mají pro všechna složení Arrheniovský tvar. Hodnoty aktivační energie a předexponenciálního faktoru stanovené pro skla s vysokým obsahem V_2O_5 jsou nižší než hodnoty pro vysoce iontovou oblast. Izotermní změny vodivostní v závislosti na složení ukazují hluboké minimum pro molární poměr x blízký hodnotě 0,65. Na obou stranách tohoto minima je vodivost převážně elektronová ($x < 0.6$) nebo iontová ($x > 0.8$). Změny vodivostní jsou interpretovány s předpokládaným převažujícím zředňovacím efektem nepřevažujícího oxidu bez interakce mezi nosiči náboje.