Materials Science-Poland, Vol. 24, No. 1, 2006

Mixed electronic-ionic conductivity in vanadate oxide glasses containing alkaline ions

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The conductivity of glasses in $50V_2O_5$–$(50–x)P_2O_5$–xA_2O (A = Li, Na, K, Rb) systems was investigated as a function of composition. In vanadate-phosphate glasses containing various alkali ions, the conductivity decreases with increasing alkali ion content. The decrease in conductivity is larger for heavier alkali ions and reaches more than seven orders of magnitude in the case of glass containing 40 mol % of Rb_2O. Only glasses containing lithium exhibit relatively small conductivity changes – less than one order of magnitude – and an increase for high lithium contents.

Key words: *glass; electronic-ionic conductivity*

1. Introduction

Electrical properties of oxide glasses containing large amounts of transition-metal ions are determined by their presence in two different valence states. The conductivity is described by small polaron hopping between such ions [1, 2]. When an alkali oxide is added during glass preparation, one may also expect mobile alkali ions to contribute to the charge transport and mixed conductivity to be observed. Generally, ionic conductivity depends on alkali concentration and ion mobility. Assuming that the motion of alkali ions and polarons are independent, one may expect electrical conductivity to increase with increasing alkali content. Real transition metal oxide glasses containing alkali, however, exhibit various behaviours – from strong conductivity anomalies to conductivity only slightly dependent on alkali content in the glass [3, 4].

The behaviour of polarons and mobile ions depends on the role of the transition metal ions in the glass structure. One possibility is for them to be a structure modifier, the most popular examples being iron and copper ions. Studies on ac and dc conductivities in oxide glasses containing iron show that their conductivities depend only slightly on alkali contents. It is shown that replacing CaO by Na_2O in modified iron

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phosphate glasses causes only a small change in dc and ac conductivities. It seems to be characteristic of glasses containing iron oxides that the alkali ions have a small mobility being bonded to the glass network. ac conductivity studies in copper-containing glass show that a mixed polaron-ionic conductivity mechanism exists even in the absence of alkali ions. Cu(I) ions can play a double role – serve as hopping centres and also contribute to the ionic conductivity [5].

The other family of TMO glasses is based on oxides, which themselves may be glass formers: MoO_3, WO_3, V_2O_5, typical examples being: P_2O_5–V_2O_5–A_2O, P_2O_5–WO_3–A_2O or TeO_2 –V_2O_5–A_2O glasses (where A is an alkali ion). Although their onductivities change significantly with the alkali content, the changes are usually non-monotonic and have anomalies and minima somewhat resembling the mixed alkali effect. Such behaviour has been observed by Bazan et al. [7] in P_2O_5–WO_3–Li_2O glass (minima of four orders of magnitude in conductivity at 10% Li_2O) and by Jayasinghe et al. [8] in TeO_2–$x$$Li_2O$–$(1–x)V_2O_5$.

The aim of the present study was to investigate mixed electronic-ionic conductivity in vanadium-phosphate glasses containing various alkali ions. In order to keep transition metal oxide contents at the same level, we prepared glasses containing the same amount of V_2O_5 and changed the ratio of P_2O_5 to Li_2O, Na_2O, K_2O or Rb_2O.

2. Experimental

Glasses of composition $50P_2O_5$–$(5O–x)V_2O_5$–xA_2O, where A = Li, Na, K, or Rb, were prepared by the conventional melt quenching technique in air with an alumina crucible. The contents of V^{4+} and V^{5+} ions were determined by chemical analysis.

Great attention has been paid to the electrode preparation process. Golden electrodes with guard rings were evaporated on polished surfaces of the samples, which had been preheated to about 150 °C in high vacuum.

Impedance measurements were carried out with a frequency response analyser Solartron 1250 and a custom trans-impedance amplifier in the frequency range from 10^{-4} to 6.5×10^4 Hz. The intrinisic Gnuplot program (www.gnuplot.org) and a Marquardt –Levenberg minimisation procedure were used for complex non-linear fitting of the impedance model parameters.

3. Results

Figure 1 shows the dependence of the amount of V^{4+} ions on the total amount of vanadium in all the studied glasses; V^{4+} content decreases on increasing the alkali content. This decrease is more pronounced when more massive alkali ions are added to the mixture, and leads to V^{4+} content being only about 11% in the case of 40% Rb. It has been reported that in binary vanadium-phosphate glass the ratio V^{4+}/ V_{tot} is in the range 0.35–0.5.

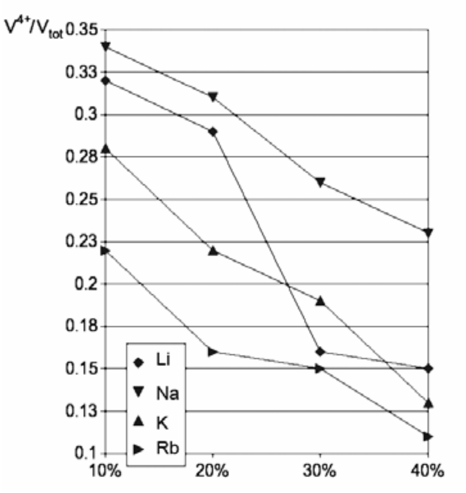

Fig. 1. The ratio of the amount of V^{4+} ions to the total amount of vanadium for various alkali contents

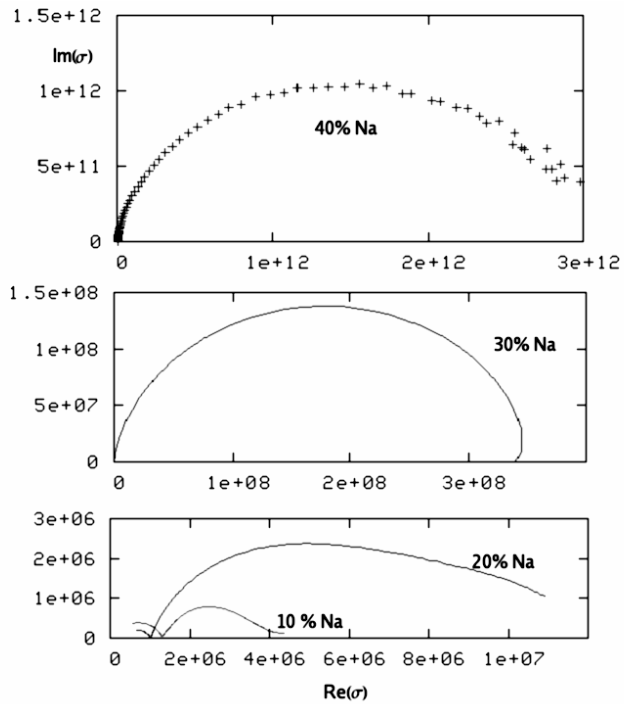

Fig. 2. The resistivity Cole–Cole plots for samples containing from 10 to 40 mol % of Na_2O in the frequency range 10^{-3}–6.5×10^4 Hz

Figure 2 shows complex plots of impedance (Cole–Cole plots) for samples containing from 10 to 40 mol % of Na_2O in the frequency range from 10^{-3} to 6.5×10^4 Hz.

A significant drop in conductivity is visible on increasing alkali content. This trend is characteristic of all families of glasses except those containing lithium, where changes in conductivity are far less pronounced. In order to obtain bulk dc conductivity, the impedance spectra were modelled by two section R-CPE (constant phase element) Maxwell [8] equivalent electrical circuits, and by single R-CPE circuits in the cases of only one semicircle plot. Parameters of the equivalent circuits were obtained directly from the measured impedance data by complex non-linear least squares fitting.

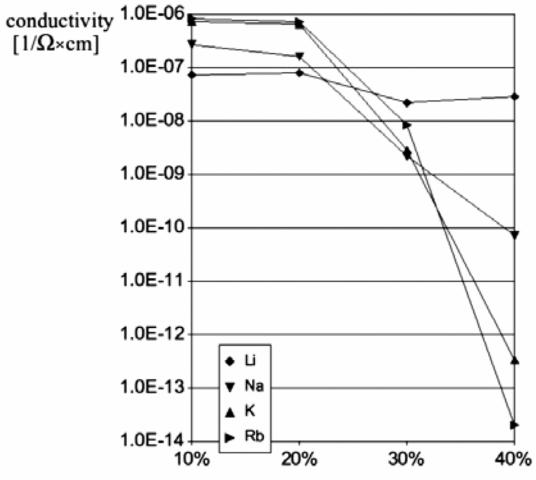

Fig. 3. Bulk dc conductivity of the glasses versus alkali content

Figure 3 presents the bulk dc conductivity versus alkali percentage for all glasses. The decrease in conductivity with increasing alkali content is larger for heavier alkali ions and reaches more than seven orders of magnitude in the case of rubidium. Only glasses containing lithium exhibit relatively small conductivity changes, of less than one order of magnitude, and an increase for large lithium contents.

4. Discussion

Several authors have observed pronounced conductivity minima in TMO glasses in certain alkali admixtures, resembling somewhat the mixed alkali effect. Such behaviour has been observed by Bazan et al. [6] who explained it by ion-polaron interaction. Jayasinghe et al. [7] have also observed this phenomenon and postulated the breaking of percolation paths. Another possibility is a significant change in the concentration ratios of transition metal ions in different valence states, since polaronic conductivity is proportional to the product of the number of ions in both valence states.

Most observations have been based on glasses in which alkali ions were substituted for transition metal ions [7, 9]. Our glasses contain large constant amounts of TMO. V_2O_5 itself is a glass former and we can substitute P_2O_5 with alkali without destroying the glass structure. This changed the variation of conductivity with increasing alkali content, especially in the case of heavy alkali ions. With increasing alkali ion content, polaronic transport is blocked at least in the case of ions heavier than lithium. This cannot be a simple dilution effect, because the concentrations of transition metal atoms remain constant. Such a large drop in conductivity also cannot originate from a change in vanadium valence.

It seems that heavy alkali ions are not mobile in vanadate glass networks and that ionic conductivity cannot develop in the high-alkali region, in contrast to glasses in which the main glass forming component is P_2O_5 and significant ionic conductivity is observed at high alkali concentrations. Recently, Ungureanu et al. [9] have found that $50P_2O_5–50[(1–x)V_2O_5–xNa_2O]$ glass exhibits a deep minimum for $x = 32.5$ mol % of V_2O_5. It is interesting that for similar glass compositions, the internal friction reveals a large peak, similar to the “mixed alkali peak” in mixed-alkali glasses [10]. Two relaxation peaks connected with electronic and ionic transport were observed in $P_2O_5–V_2O_5–Na_2O$ glasses [11].

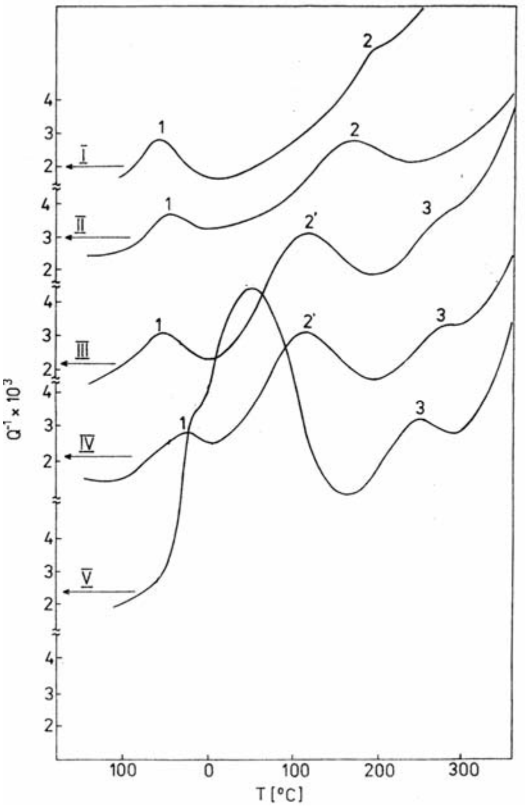

Fig. 4. Internal friction spectra for $50P_2O_5–(50–x)V_2O_5–xNa_2O$ glasses; $x = 0$ (I), 7.5 (II), 12.5 (III), 17.5 (IV), 30 mol % (V) [11]

Figure 4 shows the internal friction spectra for several vanadium-phosphate glasses doped by Na_2O. For glasses containing less than 10 mol % of Na_2O (curve I and II), the internal friction spectrum consists of two peaks: a low-temperature peak

(1) and a high-temperature peak (2). Peak 1 is related to the hopping of polarons between V^{4+} and V^{5+} ions, and its activation energy is similar to that of dc conductivity in vanadate-phosphate glasses. The high-temperature peaks 2 and 3 depend on the water content and are caused by the interaction between protons and non-bridging oxygen atoms [12]. For glasses containing more than 10 mol % of Na_2O, another peak (2′) appears above peak 1. This peak can be attributed to the migration of sodium ions. Peaks (1) and (2′) are best separated for glasses containing 12.5 and 17.5 mol % of Na_2O. It is found that the activation energy of peak 2′ is comparable with that of dc conductivity observed in sodium phosphate glasses. For 30 mol % of Na_2O these two peaks overlap and a large mixed electronic-ionic peak appears in the internal friction spectrum. Its high intensity indicates that we still have a high number of mobile ions and polarons in the glass and a deep minimum in conductivity is observed. This effect can be explained based on ion-polaron interaction. By the internal friction method it is possible to observe the relaxation of neutral ion-polaron pairs which can contribute to the broad mechanical loss peak. In the light of the experiments described above, one can suppose that in our glasses polaron-ion interaction is responsible for the strong conductivity decrease with increasing alkali ion content. As shown in Figure 2, however, this effect depends on the size of the alkali ions. We believe that the ion-polaron interaction alone cannot describe the drop in conductivity by seven orders of magnitude in Rb_2O-containing glasses. Breaking of polaron percolation paths and a very low mobility of heavy alkali ions seem to be relevant in such a dramatic change in conductivity.

5. Conclusions

The electrical properties of $50V_2O_5–(50–x)P_2O_5–xA_2O$ glasses were investigated using impedance spectroscopy. In vanadium-phosphate glasses containing various alkali ions, the conductivity decreases with increasing alkali ion content. The decrease in conductivity is larger for heavier alkali ions and reaches more than seven orders of magnitude in the case of glasses containing 40 mol % of Rb_2O. The alkali ions used are not mobile in the vanadate glass network. Only glasses containing lithium show relatively small conductivity changes – of less than one order of magnitude – and an increase for large lithium contents; these glasses also exhibit the largest mixed electronic-ionic conductivity. Admixtures of alkali ions heavier than Li block polaronic transport in vanadate-phosphate glasses.

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Received 23 December 2004
Revised 15 July 2005