

Influence of the structure of vanadate-phosphate glasses containing alkali ions on their polaronic conductivity

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Transition metal oxide glasses containing alkali show strong anomalies in conductivity of several orders of magnitude at certain amount of alkali ions. There is no general consensus on the origin of this specific shape of conductivity. The aim of the present work is to give some clue on mechanisms of conductivity anomalies in vanadate-phosphate glasses containing alkali ions. Electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) vanadium spectra were measured and compared in glasses of the $50\text{V}_2\text{O}_5-(50-x)\text{P}_2\text{O}_5-x\text{A}_2\text{O}$ ($\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$) system. A possible change of local environment of V^{+5} ions from squared pyramid to tetragonal was suggested to cause the anomalies of conductivity.

Keywords: vanadate-phosphate glasses, mixed conductivity, ion-polaron interaction.

1. Introduction

Many glasses containing a large amount of transition metal oxides are electronic conducting semiconductors. Their electrical conductivity is determined by the presence of transition metal ions in two different valence states. Their conductivity is described by a mechanism of small polaron hopping between such ions [1, 2]. The carrier concentration is constant and related to the concentration of transition metal ions in different valence states. When alkali ions are added during preparation of the glass they also take part in the conductivity process and mixed conductivity phenomena are observed. Ionic conduction generally depends on the alkali concentration and mobility of carrier ions. Assuming that the motion of alkali ions and the motion of polarons are independent of each other, one may expect that the electrical conductivity should increase with the content of alkali. However, real transition metal oxide glasses containing alkali show much variable electrical behavior. It ranges from strong anomalies in conductivity of several orders of magnitude at certain amount of alkali ions to conductivity only very little dependent on alkali content [3, 4].

In the process of glass forming most transition metal oxides may play a role of glass formers and their ions are built into the structure network. MoO_3 , WO_3 , V_2O_5 are examples of such oxides. Model glasses are: $\text{P}_2\text{O}_5-\text{V}_2\text{O}_5-\text{A}_2\text{O}$, $\text{P}_2\text{O}_5-\text{WO}_3-\text{A}_2\text{O}$,

$P_2O_5-WO_3-A_2O$ or $TeO_2-V_2O_5-A_2O$ (where A is an alkali ion). The conductivity changes very significantly with alkali contents, the observed changes being usually not monotonic, and shows anomalies and conductivity minima in a manner somewhat similar to mixed alkali effect. Such behavior was observed by BAZAN *et al.* [6] in $P_2O_5-WO_3-Li_2O$ glass (minimum four orders of magnitude in conductivity at 10% Li_2O) and by JAYASINGHE *et al.* [7] in $TeO_2-xLi_2O-(1-x)V_2O_5$.

The aim of the present study was to find some clue on interaction between electron and ionic conductivity in vanadium-phosphate glasses containing different 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 (in mol%) $50V_2O_5-(50-x)P_2O_5-xA_2O$, where A = Li, Na, K, Rb were prepared by the conventional melt quenching technique. The melting of glass was conducted in air atmosphere in an alumina crucible.

Samples of glass from the same batch were used for determination of the contents of V^{4+} and V^{5+} ions by wet chemistry method and the impedance measurements described elsewhere [8]. The NMR spectra measurements were conducted at magnetic field of 4.7 T and centre frequency of 52.6 MHz.

3. Results and discussion

Figure 1 displays the NMR spectra of glasses containing lithium. It can be seen that the spectrum obtained for 10% glass exhibits one well pronounced maximum at chemical shift of about -300 ppm and one small at about -700 ppm. With an increase

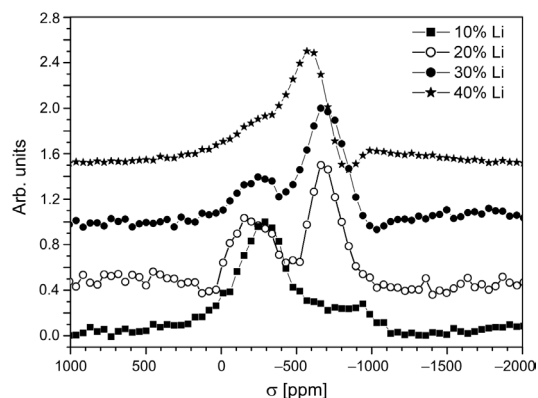


Fig. 1. NMR spectra of $50V_2O_5-(50-x)P_2O_5-xLi_2O$ glasses. The subsequent plots are shifted by a value of 0.2. The lines are intended as a guide for an eye only.



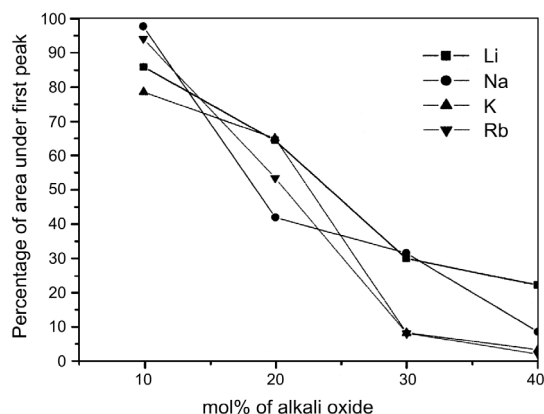


Fig. 2. Relative area under first NMR spectra maximum for $50\text{V}_2\text{O}_5-(50-x)\text{P}_2\text{O}_5-x\text{A}_2\text{O}$ glasses. The lines are intended as a guide for an eye only.

in alkali addition the first maximum decreases and the second increases (and there may be inconsiderable shifts). Essentially similar results were obtained for all alkali admixtures. Both maxima were fitted with Lorenz curves and areas under both peaks were calculated. Figure 2 shows the percentage of area under the first peak versus alkali contents for all measurement samples. Complex research on NMR spectra and comparison of various vanadates were performed by NABAVI *et al.* [13]. It shows that for compounds containing fourfold coordinated vanadium ions chemical shift varies in the range from -700 to -500 ppm. The range from -350 to -200 ppm is characteristic of square pyramidal structural units of vanadium.

Several authors observed pronounced conductivity minima in TMO glasses at certain alkali admixture in a manner somewhat similar to mixed alkali effect. Such behavior was observed by BAZAN *et al.* [6] and explained by ion-polaron interaction. JAYASINGHE *et al.* [7] also observed this phenomenon and postulated breaking the percolation paths. Another possibility is a significant change in the ratio of concentration of transition metal ions in different valence states, since the polaron conductivity is proportional to the product of amounts of ions in both valence states.

Most of the observations were made for glasses in which alkali ions were substituted for transition metal ions [7, 9]. Our glasses contain large and constant amount of TMO. This is possible because 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 picture of conductivity variations [8]. With increase in alkali content the polaron transport is blocked and conductivity decreases. In the case of heavy alkali ions it cannot be compensated for by ionic transport and a large monotonic decrease in conductivity is observed.

On the basis on the IR spectroscopy, DIMITROV [10] suggested that an introduction of alkali ions into the vanadate matrix of glass causes a destruction of its layered

structure and a development of tetrahedral units. A similar conclusion was drawn by NISHIDA and TAKASHIMA [11] on the basis of the Mossbauer spectroscopy of iron atoms introduced as probes in vanadate-phosphate glass. On the other hand, JORDAN and CALVO [12] on the basis of X-ray spectroscopy and measurements of transport properties suggested that the hopping of polarons in phosphate oxide glasses does not take place between vanadium ions in the tetrahedral environment.

DIMITROV [10] and NISHIDA and TAKASHIMA [11] observations are consistent with our NMR spectra measurements. We believe that an admixture of alkali changes local structural units of vanadium from square pyramids to tetrahedral, thus preventing a large part of vanadium ions from the conductivity process. This causes a large decrease in conductivity and this process is more pronounced in glasses containing the heaviest alkali atoms.

4. Conclusions

The NMR spectra of $50V_2O_5-(50-x)P_2O_5-xA_2O$ glasses were investigated and exhibited a systematic change in shape with an increase in alkali contents. We believe that this change is caused by a change of vanadium structural unit from square pyramid to tetrahedral.

A large decrease in hopping conductivity observed in these glasses may be caused by the exclusion of part of vanadium ions from the polaron hopping process due to this structural change.

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