

Electronic-Ionic Conductivity in Molybdenum Oxide glasses Doped with Sodium ions

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The conductivity of three glasses samples in $30\text{Na}_2\text{O}-(70-x)\text{MoO}_3-x\text{P}_2\text{O}_5$ systems and two glass samples in $60\%\text{Na}_2\text{O}-40\%\text{P}_2\text{O}_5$ and $60\%\text{MoO}_3-40\%\text{P}_2\text{O}_5$ systems was investigated as a function of temperature. It is also found that conductivity for glasses containing higher percentage of sodium ions is predominantly ionic and in glasses containing higher percentage of molybdenum ions is predominantly electronic. For pure sodium phosphate glass or the glass containing lower concentration of molybdenum the plot of $\log\sigma_{dc}$ vs. $1000/T$ is almost linear, whereas for glasses containing increasing concentration of molybdenum ions the plots depart from linearity. These non-linear plots indicate a change in activation energy which suggests a contribution from electronic conduction. Ionic glasses exhibit only one conduction process and single activation energy in the whole temperature range. In transition metal oxide glasses with mobile cations, different conduction processes contribute to electronic conduction at different temperature ranges leading to different values of activation energy. Choosing proper doping levels allows one to tailor mixed conducting oxides.

Key Words: ionic conductivity, electronic conductivity, glasses, temperature, transition metal oxide.

INTRODUCTION

In transition metal ion oxide glasses conductivity is due to small polaron hopping. The carrier concentration is related to the concentration of transition metal ion in different valence states. Several TMI glasses $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ ^{1, 2}, $\text{V}_2\text{O}_5\text{-TeO}_2$ ³, $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$ ⁴, $\text{CuO-P}_2\text{O}_5$ ⁵, $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ ⁶ and $\text{WO}_3\text{-P}_2\text{O}_5$ ⁷ have been studied and they exhibit electronic conduction. Electrical conductivity of alkali oxide glasses is known to be ionic^{8,9}. When an alkali oxide is added, mobile alkali ions will contribute to the charge transport and mixed conductivity is observed. Generally, ionic conduction depends on the alkali ion concentration and alkali ion mobility. Recently mixed electronic-ionic conductivity have been studied in vanadate oxide glasses containing alkaline ions and in iron-phosphate glasses containing sodium ions^{10,11}. The aim of the present study was to investigate

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electrical properties of the molybdenum phosphate glasses containing sodium ions, exhibiting in general, mixed ionic and electronic conduction with predominance of ionic or electronic component depending on composition.

EXPERIMENTAL

Five samples of various compositions of sodium-molybdenum phosphate glasses were prepared from NaNO_3 (Ar, E.Merck, FRG) MoO_3 (Lab Chemicals, England) and P_2O_5 (Fluka Puram) by melting in a platinum crucible in air for 1 hour at 1100°C . The melt was quenched on a brass plate preheated to about 150°C . Samples thus prepared were green in colour and glassy in appearance. X-ray diffraction studies showed that the samples were amorphous. Rectangular samples having thickness of about 1 mm were shaped by grinding and polishing with emory powder of 300 grades. Samples were given a coating of silver using conducting silver paint. Samples were then annealed at the temperature of 200°C for 2 hours to stabilize the contacts, Linear V-I characteristics confirmed Ohmic contacts. A two electrode system was used for the dc conductivity measurements. DC conductivity was measured by Keithley 617 programmable electrometer. Two independent runs on each sample were made for electrical conductivity measurements. Temperature was recorded using a Newtronic S-96 temperature controller. Density of the samples was determined by the displacement method using p-xylene as a fluid.

RESULTS AND DISCUSSION

Fig.1 shows temperature dependence of d.c. (σ_{dc}) conductivity of all the investigated samples. Values of d.c. (σ_{dc}) conductivity for different compositions of glasses at 400 K are given in table 1. Values of d.c. (σ_{dc}) conductivity for molybdenum phosphate glass containing 60mol% MoO_3 is comparable to that reported by Mansingh *et al.*¹⁰. Similarly experimental values of d.c. (σ_{dc}) conductivity for sodium phosphate glass containing 60mol% Na_2O were comparable to those reported by Nasu and Soga⁸. These values should be considered comparable taking into consideration the fact that electrical properties of glasses are greatly affected by composition, thermal history and preparation conditions, and an order of magnitude agreement between the values reported by different authors may be considered reasonably good agreement.

The density of 60mol% Na_2O glass is lowest as compared to the 60mol% MoO_3 . This is due to smaller size of sodium ion (95pm) as compared to molybdenum ion (129pm). In rest of the samples the density increases with the increase of molybdenum ion concentration.

The values of d.c. (σ_{dc}) conductivity for 60mol% MoO_3 glass at any temperature is considerably lower than that for 60mol% Na_2O glass. This is due to smaller ionic size of sodium ion and small concentration of reduced state

(Mo^{5+}) of molybdenum ions. The d.c. (σ_{dc}) conductivity of 30mol% Na_2O -10mol% MoO_3 -60mol% P_2O_5 glass is larger than that of the 60mol% MoO_3 -40mol% P_2O_5 glass at all temperatures as shown in fig.1 probably because of larger ionic conductivity of sodium ions. At fixed sodium ion concentration the d.c. (σ_{dc}) conductivity has been observed to increase with molybdenum ion concentration. Critical observation reveals that in fig.1 for pure sodium phosphate glass or the glass containing 10mol% MoO_3 the plots are almost linear. This is in agreement with ionic conducting oxide glasses where conductivity obeys a simple Arrhenius dependence with constant activation energy¹². For the glasses containing increasing concentration of molybdenum ions the plots deviate from linearity. The nonlinear Arrhenius plot is also noticeable for most semiconducting oxide glasses. The non linear plots indicate a change in activation energy which suggests a contribution from electronic conduction. Ionic glasses exhibit only one conduction process and single activation energy in the whole temperature range⁸. In transition metal oxide glasses with mobile cation, different conduction processes contribute to electric conduction at different temperature range leading to different values of activation energy.

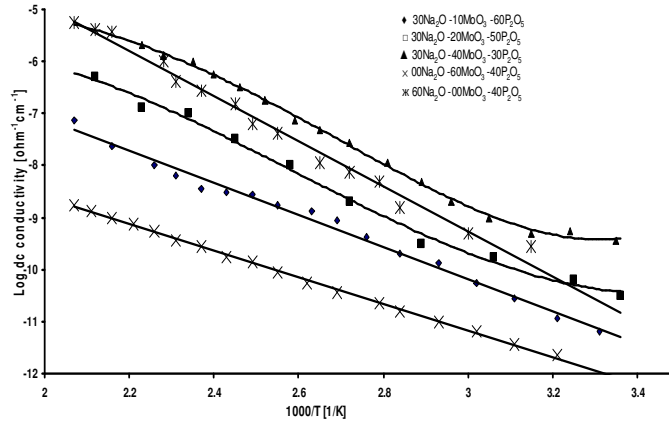


Fig.1. Temperature dependence of log dc conductivity for molybdenum phosphate glasses containing Na_2O

Table. 1. The electrical properties of Na_2O - MoO_3 - P_2O_5 glasses.

Composition (mol%)			Density	R ($^{\circ}\text{A}$)	d.c. conductivity	W
Na_2O	MoO_3	P_2O_5	(g/cm^3)		($\Omega^{-1} \text{cm}^{-1}$)	(eV)
30	10	60	2.66	9.04	2.00×10^{-9}	0.84
30	20	50	2.78	7.07	1.40×10^{-8}	0.79
30	40	30	3.28	5.32	1.58×10^{-7}	0.74
00	60	40	3.51	4.84	1.12×10^{-10}	0.59
60	00	40	2.88	--	9.95×10^{-8}	0.84

The transport of electrons in transition metal oxide glasses is usually termed as small polaron hopping. A general formula for the electrical conductivity was proposed by Mott¹³ in which the conductivity is given by

$$\sigma_{dc} = c(1-c) \frac{e^2 v_{el}}{KTR} \exp(-2\alpha R) \exp\left(\frac{-W}{KT}\right)$$

where α is the rate of the wave function decay, $v_{el} \approx 10^{15} \text{ s}^{-1}$ is the electronic frequency, C is the ratio of ion concentration in the low valency state to the total concentration of transition metal ions, N is the number of transition metal ion sites/cm³, R is the average site spacing and W is the activation energy arising from the electron-lattice interaction. The activation energy W is the sum of polaron hopping energy W_H and disorder energy W_D which might exist between the initial and final sites due to the variation in the local arrangements of ions. Austin and Mott¹⁴ have shown that

$$\begin{aligned} W &= W_H + \frac{1}{2} W_D & \text{for } T > \theta_D/2 \\ W &= W_D & \text{for } T < \theta_D/4 \end{aligned}$$

Values of activation energy W have been evaluated from the slopes of plots of $\log \sigma_{dc} T$ vs. $1000/T$ (not shown here). Values of W are given in table 1. The values of W for pure sodium phosphate glass as well as for sodium phosphate glass containing 10mol% MoO₃ is large. The large activation energy may suggest that conductivity is dominated by ionic transport. The values of W decrease with the further increase of MoO₃ concentration or with the decrease of nearest neighbour molybdenum ion separation. Values of R derived from the relation $N = 1/R^3$ are also given in table1. The decrease in activation energy with the increase of MoO₃ concentration indicates that the contribution of electronic conduction increases.

Conclusions

The d.c. electrical conductivity of sodium molybdenum phosphate glasses were investigated. The results show that the contribution of electronic conduction to d.c. conductivity increases with molybdenum ion concentration, Whereas in glasses containing higher concentration of sodium ions the ionic conduction is predominance over electronic conduction.

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Application of Nanostructures and New Nano particles as Advanced Biomaterials

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The new nanomaterials have a much larger contact surface area than the existing micro materials by using the nanoparticle control technology. . The recently developed nanostructures include nanoparticles, nanofibres and other nanomaterials like single enzyme nanoparticles (SEN) used for various applications in bioscience research from biosensors to new drug development, food, environmental monitoring, proteomics, and bio-marker analysis and in virus detection. Biological signal transducers are widely used for the manufacture of Nanobiosensors. This paper briefly describes the various nanotechnologies developed and untied in the areas of bioscience research and environmental applications and regulations to be adopted for future nanocompanies .

Key Words: Single Enzyme Nanoparticles, Nanoparticle Control Technology, Nanobiosensors.

INTRODUCTION

Recent breakthroughs in nanotechnology have made various nanostructured materials more affordable for a broader range of applications. Although we are still at the beginning of exploring the use of these materials for biocatalysts, various nanostructures have been examined as hosts for enzyme immobilization via approaches including enzyme adsorption, covalent attachment, enzyme encapsulation and sophisticated combination of these methods. This paper discusses the stabilization mechanisms behind these diverse approaches; such as confinement, pore size and volume, charge interaction, hydrophobic interaction, and multipoint attachment. In particular, we will discuss recently reported approaches to improve the enzyme stability in various nanostructures such as nanoparticles, nanofibers, mesoporous materials, and single enzyme nanoparticles (SENs). In the form of SENs, each enzyme molecule is surrounded with a nanometer scale network, resulting in stabilization of enzyme activity without any serious limitation for the substrate transfer from solution to the active site. SENs can be further immobilized into mesoporous silica with a large surface area, providing a hierarchical approach for stable immobilized enzyme systems for various applications such as bioconversion, bioremediation and biosensors.

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