Journal of Alloys and Compounds 469 (2009) 576–579

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

ac conductivity studies in single and mixed alkali vanadophosphate glasses

T. Sankarappa *, G.B. Devidas, M. Prashant Kumar, Santosh Kumar, B. Vijaya Kumar

Department of Physics, Gulbarga University, Gulbarga 585 106, Karnataka, India

Received 25 October 2007; received in revised form 29 January 2008; accepted 2 February 2008
Available online 18 March 2008

Abstract

Two different series of vanadophosphate glasses doped with sodium and sodium–potassium were investigated for ac conductivity in the frequency range 500 Hz to 500 kHz and temperature range 300–660 K. Mott's small polaron hopping has been used to explain the temperature dependence of electrical conductivity. The change over of conduction mechanism, occurring at 0.16 mole fraction of Na_2O from predominantly electronic to ionic has been observed in single alkali glasses. The mixed alkali effect, in terms of electrical conductivity and activation energies associated with it, has been observed to be occurring at 0.12 mole fraction of second alkali (K_2O) content in mixed alkali glasses. The results have been discussed.

PACS: 61.43.Fs; 72.60.+g; 84.37.+g

Keywords: Phosphate glasses; Alkali ions; Mixed conductivity; Mixed alkali effect; Mott's small polaron hopping

1. Introduction

Phosphate glasses have found many applications in optics such as laser host materials, optical filters, etc., and other areas [1,2]. Pure phosphate glasses are highly hygroscopic which limits their applications. These glasses are easy to prepare due to their low melting and glass transition temperatures. Different efforts have been made to increase the chemical durability of phosphate glasses but improvements are normally accompanied by an increased glass transition temperature [3–5]. However, the phosphate glasses doped with alkali/alkaline ions have been reported to be relatively stable and durable [6,7].

Charge transport studies in ionic semiconducting glasses have become current topic of research mainly due to their potential applications in solid-state devices. The ionic conductivity studies on various kinds of glasses have revealed their importance in the technological applications such as chemical sensors, solid-state batteries and electrolytes, etc. [8–10]. Electrical conductivity studies in sodium–vanadophosphate glasses revealed the change over of conduction mechanism from predominantly electronic to ionic [10]. The change in conduction mechanism, either from dominant ionic to electronic or electronic to ionic, has also been observed in various tellurite [8,9] and borate [11] glasses. The mixed mobile ion effects were studied in detail in Na–Ag-doped phosphotellurite glasses and the glass transition temperature has been observed to be passing through minimum [12]. The frequency dependent electrical conductivity studies in sodium–potassium–iron–phosphate glasses have been reported. The mixed alkali effect detected in these systems has been attributed to the interactions between alkali ions.

In the present communication, we study the ac conductivity in two different series of vanadophosphate glasses in the following mentioned compositions;

i. $(V_2O_5)_{0.3-x}$ $(P_2O_5)_{0.7}$ $(Na_2O)_x$; (x = 0.10, 0.12, 0.14, 0.16, 0.18 and 0.20) labeled as SN1, SN2, SN3, SN4, SN5 and SN6.
ii. $(V_2O_5)_{0.2}$ $(P_2O_5)_{0.6}$ $(Na_2O)_{0.2-x}(K_2O)_x$; (x = 0.04, 0.08, 0.12, 0.16) labeled as M1, M2, M3 and M4.

Though, the glasses labeled as SN above have been explored for dc conductivity studies earlier [10], the objective of the present investigation is to study the frequency dependence of electrical conductivity and reconfirm the change over of conduction mechanism reported in Ref. [10]. The mixed alkali glasses

* Corresponding author. Tel.: +91 8472 263298; fax: +91 8472 263206.
E-mail address: sankarappa@rediffmail.com (T. Sankarappa).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2008.02.012

mentioned above were chosen to investigate the MAE in the presence of transition metal ions and these glasses have not been previously explored for the properties studied here.

2. Experimental

The vanadophosphate glasses doped with single and mixed alkali ions were prepared by melt-quenching technique using analytical grade vanadium pentoxide (V_2O_5), lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$). The relevant chemicals in appropriate weight ratios were taken in a porcelain crucible and melted in a muffle furnace at 1400 K. The melt was quickly quenched by pouring on a stainless steel plate and covering with another stainless steel plate. The random pieces of the glass samples thus formed were collected. In order to relieve mechanical stresses, the samples were annealed at 650 K. The glassy nature of samples was confirmed by XRD studies.

The frequency dependent measurements of capacitance, C, and dissipation factor, $\tan\delta$, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies in the range 500 Hz to 500 kHz and temperature from 300 K to 660 K. The dielectric constant (ε'), dielectric loss factor (ε'') and ac conductivity (σ_{ac}) were determined as per the following expressions:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

$$\varepsilon'' = \varepsilon' \tan\delta \quad (2)$$

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon'' \quad (3)$$

where, ε_0 is the permittivity of free space, d is the thickness of the glass sample and A is cross-sectional area of the sample.

3. Results and discussion

3.1. SN glasses

The temperature dependence of ac conductivity at different frequencies for all SN glasses has been analyzed and a typical plot for SN2 glass is depicted in Fig. 1. From this figure, it is clear that the ac conductivity increases with increase in frequency. Similar results have been obtained for all remaining

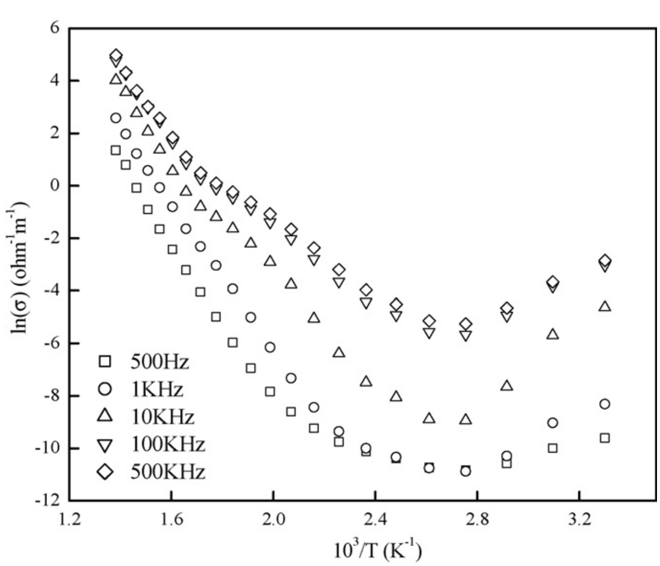

Fig. 1. Temperature dependence of ac conductivity at different frequencies, for the glass SN2. Solids lines are the least square linear fits to the high temperature data.

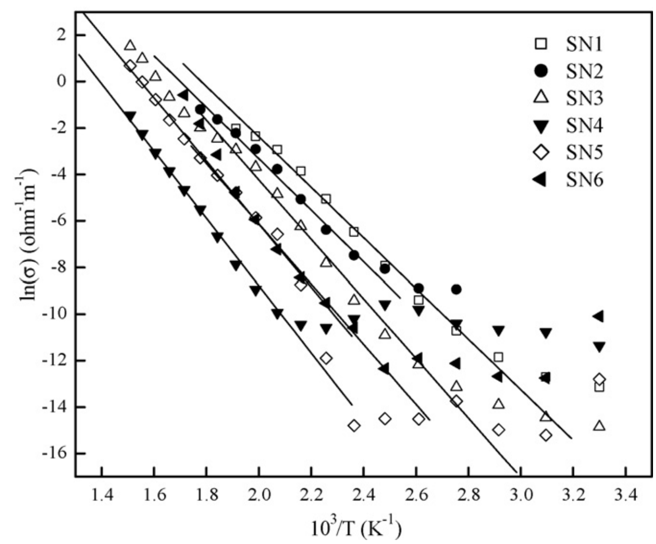

Fig. 2. Temperature dependence of ac conductivity at 10 kHz for SN glasses. Solids lines are the least square linear fits to the high temperature data.

SN glasses. The temperature dependence of ac conductivity at 10 kHz for all SN glasses is shown in Fig. 2. The conductivity was found to increase with increase in temperature, which reveals the semiconducting nature of the present glass samples. Within the studied frequency range and temperature, the ac conductivity varied in the range from 10^{-2} ohm^{-1} m^{-1} to 10^{-6} ohm^{-1} m^{-1} for SN glasses. These conductivity ranges are in agreement with the reported ac conductivities on similar and other glass systems [4–12].

Further, at all studied frequencies and temperatures, SN glasses exhibited decrease in electrical conductivity with increase in Na_2O ion concentration up to 0.16 mole fraction and increased for further doping of Na ions. This behavior hints at the change over of conduction mechanism from predominantly electronic to ionic at around 0.16 mole fraction of Na_2O [10].

The variation of conductivity was observed to be a thermally activated process and is due to the hopping of polarons [13]. The temperature dependence of conductivity has been considered in the light of Mott's small polaron hopping model. Based on diffusion model, Mott [14] has discussed the conduction process in terms of hopping of electrons between localized states and proposed an expression for the electrical conductivity in semiconducting glasses:

$$\sigma = \frac{\upsilon_0 e^2 C(1-C)}{k_B T R}\exp(-2\alpha R)\exp\left(\frac{-W}{k_B T}\right) \quad (4)$$

where υ_0 is the characteristic phonon frequency, α is the rate of wave function decay, C is the ratio of ion concentration in low valence state to total concentration of transition metal ions, R is the average hopping distance, W is the activation energy, e is the electronic charge, k_B is the Boltzamann constant and T is the absolute temperature.

Eq. (4) describes a non-adiabatic regime of small polaron hopping and is usually used to analyze the electrical conductivity of glasses containing transition metal ions. The non-adiabatic term $\upsilon_0\exp(-2\alpha R)$ describes the probability of an electron tun-