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Electronic-Ionic Conductivity of Lithium-Vanado- Phosphate Glasses

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Abstract

The new glassesof glass system x Li_2O-50 V_2O_5-(50-x) P_2O_5 were prepared by using conventional melt quenching method. The densities of these glasses have been measured by Archimedes method and corresponding molar volumes have also been calculated. The conductivity of these glasses was measured as a function of temperature and composition. The variations of conductivity versus temperature follow Arrehenius type relationship. Conductivity decreases with increasing Li_2O content and increase with increasing temperature. The calculated activation energy decreases up to 15mol% of Li_2O, it increases from 15mol% to 30 mol% of Li_2O and again it suddenly drops at 40 mol% of Li_2O. This may be due to structural changes in glass network and these glasses exhibit both electronic and ionic conductivity.

Keywords: Density; Conductivity; Activation energy; Phosphate glass.

1. Introduction

Vanado-Phosphate glasses containing alkali ions exhibit mixed electronic- ionic conduction [1], which depending upon the proportions of transition metal ions (TMI), can be purely electronic (high TMI), purely ionic (low TMI) or intermediate electronic-ionic [2]. Generally, ionic conductivity depends on alkali concentration and ion mobility. In some glasses conductivity changes

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significantly with the alkali content, the changes are usually monotonic [3,4]. Ionic conduction in these glasses occurs via the motion of Li^+ ions, while electronic transport takes place by polaron hopping between V^{4+} and V^{5+} centers present in glass network [5]. Assuming that the motion of alkali ions and polarons are independent, one may expect electrical conductivity to increase with increasing alkali content. The possibility of controlling the character of conductivity within the same system by adjusting chemical composition can be of interest for potential applications of these conductors as basic components in integrated micro-batteries, solid electrolytes and mixed electronic-ionic cathode materials [6].

2. Experimental Procedure

Glasses of composition x Li_2O– 50 V_2O_5- (50-x) P_2O_5 where x = 5,10,15,20,30 and 40 mol% were prepared by conventional melt quenching method. Analytical grade ammonium dihydrogen orthophosphate, Lithium carbonate and vanadium pentaoxide chemicals were used as starting materials. The detailed experimental procedure was explained elsewhere [7]. Suitable samples were selected for electrical measurements. The resistance of the sample was measured by applying a dc field of 5V and the current through the sample was measured using digital electrometer (ECIL EA-5600). The temperature was measured by using a "Chromel-Alumel" thermocouple placed very close to the sample. The temperature dependence of conductivity of this glass system was measured in the temperature range 348 – 507 K.

The densities of these glass samples were measured by Archimedes method using toluene as an immersion liquid (Density = 0.86 g/cm^3 at room temperature). The corresponding molar volumes (V_m) were calculated by using the relation $V_m = M/\rho$, where M is molecular weight and ρ is the density of corresponding glass samples.

3. Results and Discussion

Figure 1 shows the variation of density versus mol% of Li_2O, the densities of these glasses increases with increasing Li_2O content. This indicates that by addition of Li_2O into glass network, it may resist the creation of non- bridging oxygens, hence the density increases. As can be seen from figure 2, the molar volume of these glasses decreases with increasing concentration of Li_2O is expected.

Figure 3 shows the temperature dependence of conductivity of lithium-vanado-phosphate glasses. It also represents the Arrhenius plot of the conductivity variations as a function of temperature. In this glass system with increasing Li_2O content conductivity decreases it may be due to blocking of polaronic transport. This cannot be a simple dilution effect, because vanadium concentration remains constant. It seems Li^+ ions are not mobile in vanadate glass network and ionic conductivity cannot develop at high Li_2O content region [8]. As can be seen in figure the change of slope occurs depends on the chemical composition of the glass. The changes in slopes of temperature dependences of conductivity of these glasses suggests that the character of conductivity not only on composition but also on temperature [6]. A drastic change in slope can be observed at 30 mol% of Li_2O, may be due to structural change in glass network at this composition. The activation energies determined in these glasses are in the range of 0.45 eV to 0.79 eV. The activation energy decreases up to 15mol% of Li_2O, it increases from 15 mol% to 30 mol% of Li_2O and again it suddenly drops at 40 mol% of Li_2O as shown in figure 4. According to M.C.Ungureanu et al [9] Activation energy, if it lies around 0.5 eV is electronic and if it is close to 0.75 eV is ionic conductivity. As can be seen from the table 1, activation energy is around 0.5 eV except at 5 and 30mol% Li_2O is greater than 0.5 mol%. It indicates that these glasses exhibit ionic conductivity only at 5 and 30 mol% Li_2O concentration and exhibits electronic conductivity at other than these compositions. Due to constant concentration of V_2O_5 throughout the system the predominance V^{5+} centers electronic conductivity is expected but at 5 and 30 mol% of Li_2O it may be due to the predominance of V^{4+}centers strong disruption of the glass network, electron hopping is unlikely and the total conductivity is due to ionic transport [10].

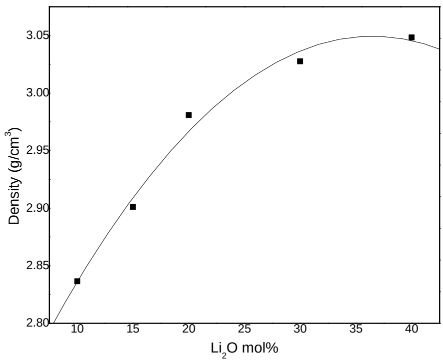

Fig 1.Variation of density versus Li_2O mol%.

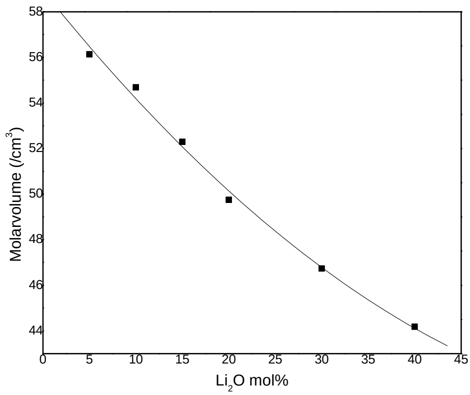

Figure 2.Variation of molar volume versus Li_2O mol%.

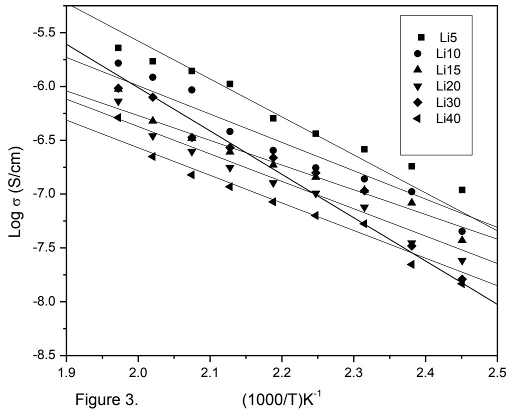

Fig 3.Conductivity variations as a function of temperature.

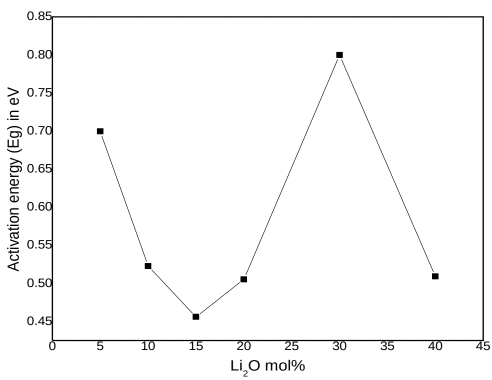

Fig 4.Variation of activation energy versus Li_2O mol%.

4. Conclusion

The electrical conductivity of x Li_2O – 50 V_2O_5 - (50-x) P_2O_5 glasses was investigated as a function of temperature and composition. Conductivity decreases with increasing Li_2O content and increase with increasing temperature. The activation energy decreases up to 15mol% of Li_2O, it increases from 15mol% to 30mol% of Li_2O and again it suddenly drops at 40mol% of Li_2O. This may be due to structural changes in glass network and these glasses exhibit both electronic and ionic conductivity.

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