Investigation of the conductivity of the vanadium phospoborate glass system

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We investigated DC conductivity in $60V_2O_5$–(40-x) P_2O_5–x B_2O_3 glasses as a function of temperature. The measurements were carried out in a temperature range of 302–473 K. For all compositions, the DC conductivity increased with the increasing B_2O_3. The increase in conductivity was more pronounced due increased in number of non-bridging oxygens (NBOs). The maximum value of conductivity was found to be 9.85×10^{-4} Scm^{-1} at 473 K for 35 mol % of B_2O_3. Tg and T_c was found to be 110 ºC and 140 ºC respectively for 35 mol % of B_2O_3. The ionic conductivity was found to be dominant over the electronic conductivity.

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1. Introduction

Ionic conductivity of binary and ternary glassy systems has been comprehensively studied in the earlier period due to their probable use in solid state devices. Glasses are technologically significant materials due to its better thermo-mechanical, electrical and physico-chemical properties, which make them appropriate for use in vacuum, high-voltage, and biomedical applications [1]. Several transition metal ion oxide TMO glasses like V_2O_5-P_2O_5, V_2O_5-B_2O_3, Fe_2O_3-P_2O_5 and WO_3-P_2O_5 have been studied and they exhibit electronic conduction, which is known to be ionic [2]. In recent times mixed electronic-ionic conductivity has been studied in vanadate oxide glasses and in phosphate glasses [3]. TMO doped alkali borate glasses have been the focus in the recent years in view of their several applications in different domains of modern technology [4].

DC conductivity of vanadium oxide glasses in which V_2O_5 is associated with other glass formers such as P_2O_5 has been extensively studied. These studies have shown that the small polaron hopping model describe the electronic transport phenomena in these materials [5]. Borate glasses with alkali ions are considered as important materials in microelectronics, optics and in optical fibers due to its scientific and technological application. The structure of pure B_2O_3 consists of a random network of boroxol rings and BO_3 triangles connected by B–O–B linkage [6]. Phosphorus pentaoxide (P_2O_5) glasses have a number of advantages over usual silicate glasses due to its better physical properties such as high thermal expansion coefficients and low melting temperatures [7, 8].

The purpose of this work was to investigate the DC electrical and thermal properties of $60V_2O_5$–(40-x) P_2O_5–x B_2O_3 glass systems. The characterization technique, thermo gravimetric-differential thermal analysis (TG-DTA) and x-ray diffraction (XRD) is employed to study the structural properties of glass samples.

2. Experimental

The glass samples of compositions (in mol %) of $60V_2O_5$–(40-x) P_2O_5–x B_2O_3, x = 5, 10, 20, 30 and 35 were prepared by melt-quenching method. The AR grade chemicals were weighed and mixed together. This mixture was homogenized and the melting of glass was conducted in air atmosphere in silica crucible in a furnace at a temperature1200 K for 3 h and the melt was stirred to remove CO_2. After melting, the mixture was poured out onto a nonmagnetic stainless steel plate. The sample was characterized by using XRD and TG-DTA techniques. The XRD pattern of powder sample was recorded on a XRD Philips PW 1830 using CuK_α radiation in the range 10°−60°. The TG-DTA was carried out on Shimadzu DTG-60h thermal analyser under nitrogen flow.

Much concentration was given to the electrode preparation process. The samples were polished and silver electrode was deposited on both sides of the samples. The electrical conductivity measurements (temperature dependence of DC conductivity (σ)) were conducted using two probe techniques. The measurements were performed in a temperature range of 302–473 K. The temperature was controlled with a programmable oven. The electronic contribution to the total conductivity (Transference number measurement) for all samples was determined using Wagner's dc polarization technique by depositing blocking electrode on both sides of the samples.

3. Result and discussion

3.1 XRD analysis

Fig. 1 shows the usual XRD patterns of $60V_2O_5$–(40-x) P_2O_5–x B_2O_3, x = 5, 10, 20, 30 and 35 mol %. As there was no distinguishing peak which corresponds to any crystalline stage, therefore it can be inferred that the prepared samples are amorphous in nature.

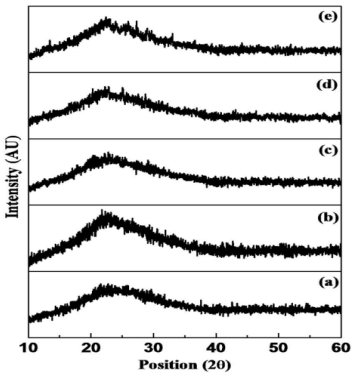

Fig. 1. XRD of $60V_2O_5$–(40-x) P_2O_5-xB_2O_3 for (a) x=5 mol %, (b) x=10 mol %, (c) x=20 mol %, (d) x=30 mol % and (e) x=35 mol %.

3.2 Thermal analysis

TG-DTA analysis for 35 mol % of B_2O_3 was carried out in order to study the changes occurred regarding the phase transition during heat treatment, also to identify thermal stability of the glass samples. TGA curves are displayed in Fig. 2 show thermal dehydration in samples. From TG, weight loss of 15 % is in the temperature range of 30–200 °C which corresponds to loss of water molecules. After this a gradual loss in weight is observed till 300 °C. This may be due to the condensation of structural hydroxyl groups [9, 10].

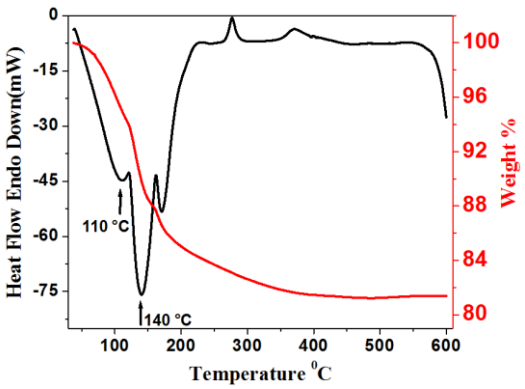

Fig. 2. TG-DTA Plots of $60V_2O_5$–$5P_2O_5$-$35B_2O_3$ glass.

From DTA curve, an endothermic peak was observed between 105 and 115 °C and may be assign for T_g. Another sharp endothermic peak between 135 and 145 °C followed by an exothermic peak may be appear due to some of the physical changes like melting or decomposition followed by amorphous to crystalline phase transition [10, 11]. T_g is 110 °C whereas, T_c is 140 °C respectively.

3.3 DC conductivity

The temperature dependence of DC conductivity in the temperature range 302–473 K is shown in Fig. 3. The DC conductivity exhibits Arrhenius-type temperature dependence. The values of σ_{dc}, E_{dc} and log σ_0 for different compositions are listed in Table 1. The variation of σ_{dc} and E_{dc} as a function of mol % of B_2O_3 is shown in Fig. 4.

It is observed that the conductivity increases with temperature and B_2O_3 contents and showed the highest conductivity of 9.85×10^{-4} Scm^{-1} at 473 K for 35 mol % of B_2O_3. The increased in DC conductivity may be due the accompanying change in chemical bonding of the glass structure, i.e., increased in number of non-bridging oxygens (NBOs) by breaking the closed bridges [12-14]. In addition, it is suggested that the increased in DC conductivity and decreased in activation energy may be due to increased in mobile ion concentration on one hand, and a decreased in the strength of glass structure, on the other hand. This enhanced conductivity may be attributed to a decreased in strength of glass structure [15, 16].

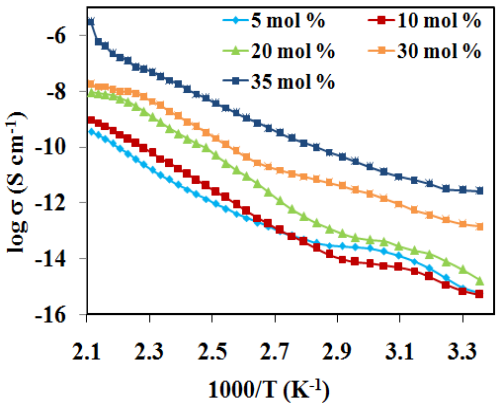

Fig. 3. Temperature dependence DC conductivity for different mol % of B_2O_3.

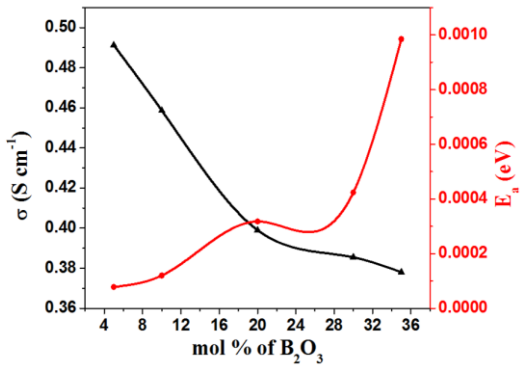

Fig. 4. Variation of σ_{dc} and E_{dc} with mol % of B_2O_3.

3.4 Transference number measurement

The t_{ion} and t_{ele} has been calculated from the plot. Fig. 5 shows the plots of current verses time for all the compositions of V_2O_5–P_2O_5–B_2O_3 glass system. The total current becomes nearly constant at some non-zero value after some time. The final residual current is mainly due to electrons/holes [17, 18]. The calculated transference number for all samples is listed in Table 1. The values of transference number are found to be in the range of 0.82 to 0.93. This suggests that the charge transport in all the samples are predominantly due to ions. For 35 mol % of B_2O_3 sample it is 0.89.

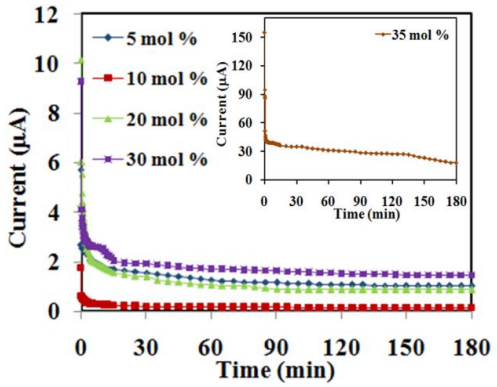

Fig. 5. Plots of DC current versus time for different mol % of B_2O_3.

Table 1. DC transport properties of $60V_2O_5$–$(40\text{-}x)$ P_2O_5-xB_2O_3 for different mol % of B_2O_3.

Mol % of B_2O_3	E_{dc} (eV)	σ_{dc} $\times10^{-4}$ at 303 K (Scm^{-1})	σ_{dc} $\times10^{-4}$ at 473K (Scm^{-1})	log σ_0	t_{ion}	t_{ele}
5	0.49	0.00225	0.785	0.702	0.82	0.18
10	0.46	0.00239	1.2	1.92	0.93	0.07
20	0.4	0.00376	3.18	4.029	0.92	0.08
30	0.39	0.0259	4.24	1.7	0.84	0.16
35	0.38	0.0934	9.85	3.305	0.88	0.12

4. Conclusions

The melt-quenching technique is a very straightforward technique used for the preparation of the conducting glasses. XRD confirms the amorphous nature of the all prepared samples. T_g and T_c was found to be 110 ºC and 140 ºC respectively for 35 mol % of B_2O_3. The DC conductivity shows Arrhenius-type temperature dependence. The DC conductivity increases, which may be due to increased in number of non-bridging oxygens (NBOs) with B_2O_3. The maximum value of conductivity and minimum value of activation energy were found to be 9.85×10^{-4} Scm^{-1} at 473 K and 0.38 eV respectively for 35 mol % of B_2O_3. The ionic conductivity was found to be dominant over the electronic conductivity and varies between 82-93%.

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