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AC conductivity and dielectric relaxation in V_2O_5–P_2O_5–B_2O_3 glasses

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ABSTRACT

We investigated the AC conductivity in $60V_2O_5$–$(40-x)P_2O_5$–xB_2O_3 (x = 5, 10, 20, 30 and 35 mol%) glasses as a function of temperature. The measurements were carried out in the frequency range from 20 Hz to 1 MHz with varying temperatures (303–473 K). The samples were characterized by using X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis (TG-DTA) techniques. The molar volume increases monotonically with the decrease in density. The AC conductivity increases with B_2O_3 content and temperature. The AC conductivity exhibited a Jonscher's universal power law and it is observed that as the temperature increases, frequency exponent (s) decreases. The dielectric constant of the sample decreases with increasing frequency and increases with temperature and concentration of B_2O_3. The electric modulus representation has been used to provide comparative analysis of the ion transport properties in these glasses. Scaling by using electric modulus shows overlap on single master curve signifying that the conduction mechanism is independent of temperature.

1. Introduction

Conducting glasses have attracted much interest in the field of solid-state chemistry and materials science. Vanadium pentoxide has a well-known structure composed of VO_5 pyramids. The glass containing V_2O_5 shows semiconducting behaviour [1]. Transition metal oxides' glasses exhibit electronic conductivity. The electrical properties of these glasses are determined by the presence of the transition metal ions and the conductivity is described by the mechanism of polaron hopping [2,3]. Borate glasses are found to be very appealing amorphous materials, which possess the particular structure and physical properties for advance applications. In these glasses, two groups of bands are obtained due to trigonal BO_3 and tetrahedral BO_4 units. The addition of transition metal ions to the borate glasses gives specific physical properties [4,5]. Only some studies have been carried out on glasses containing V_2O_5 and B_2O_3. These glasses have potential applications in optical and electrical memory switching, as cathode materials for making solid devices and as optical fibre [6,7]. Boric oxide (B_2O_3) is a prominent glass former due to its extremely viscous melt which forms at much lower temperature. Beside that, B_2O_3 glasses are strongly tied in strength due to metal-oxygen bond (B–O). The study of dielectric parameters will uncover the way to understand more about the structural environment of the glass network [8,9].

From the literature survey, it is revealed that no unified studies of vanadate–phosphate–borate (V_2O_5–P_2O_5–B_2O_3) glasses are present in the literature of material science, which comprises parameters like frequency exponent and scaling to modulus. Therefore the aim of the present work is to investigate the effect of addition of B_2O_3, temperature and frequency on the polarization state of the glass samples by means of systematic determination of conductivity, dielectric constant and modulus in the frequency range of 20 Hz to 1 MHz and temperature range of 303–473 K. The prepared glass samples were characterized through X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis (TG-DTA) is employed to study the structural and thermal properties of glass samples.

2. Experimental

The vanadate–phosphate–borate glasses in the composition of $60V_2O_5$–$(40-x)P_2O_5$–xB_2O_3, x = 5, 10, 20, 30 and 35 mol% were prepared by a usual melt-quenching method. In this investigation the AR grade chemicals were weighed and mixed together. This mixture was homogenized and melted in a silica crucible in a furnace at 900 °C for 3 h and the melt was stirred to remove CO_2. After

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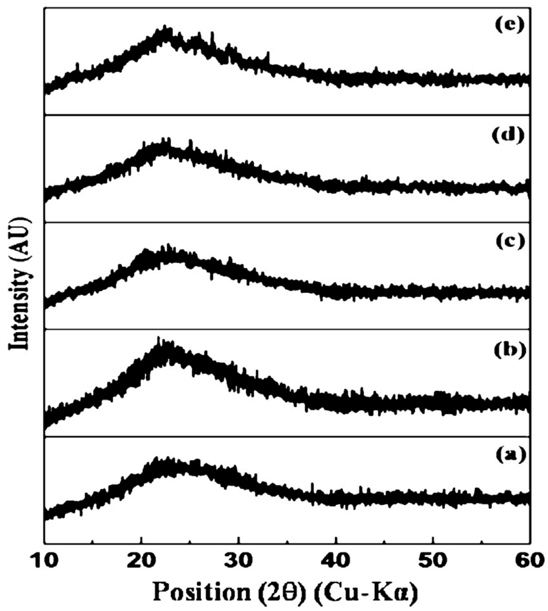

Fig. 1. XRD of $60V_2O_5$–$(40-x)P_2O_5$–xB_2O_3 glass samples for (a) $x=5$ mol%, (b) $x=10$ mol%, (c) $x=20$ mol%, (d) $x=30$ mol% and (e) $x=35$ mol% at room temperature.

melting, the mixture was poured out onto a nonmagnetic stainless steel plate so that the sample (Circular) had a thickness of nearly about 3 mm. To avoid internal strains, the sample was annealed at 200 °C for 1 h. For the electrical measurements, the samples were polished and conducting silver paste (electrode) was deposited on both sides of the samples for a radius of nearly about 3.5 mm.

The sample was characterized by using XRD and TG-DTA techniques. The XRD analysis was carried out at room temperature within $2\theta=10$–$60°$. The pattern was recorded with a step height of 0.02° and with scan rate 6.00. The TG-DTA was carried out under constant nitrogen flow with heating rate 12 °C/min.

The density of the glass samples was determined at room temperature through Archimedes principle, by using xylene. The density was estimated by using Eq. (1)

$$\rho = \left(\frac{W_a}{W_a - W_l}\right) \times \rho_l \quad (1)$$

where ρ is the density of the sample, W_a is the weight of the sample in air, W_l is the weight of the sample fully immersed in xylene and ρ_l is the density of the xylene.

The molar volume V_m was calculated from Eq. (2)

$$V_m = \frac{M_T}{\rho} \quad (2)$$

where M_T is the molecular weight of the glass.

The temperature dependence of AC conductivity (σ) and dielectric constant (ε') were measured using LCR meter, Agilent Technology, Singapore. The measurements were performed in a frequency region of 20 Hz to 1 MHz and a temperature range of 303–473 K. The electrical modulus was studied for all compositions.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows XRD pattern of all prepared glass samples. The absence of sharp Bragg's peak confirmed amorphous and homogeneous nature of glass samples. The broad hump observed in XRD pattern of all samples indicates lack of a long-range order.

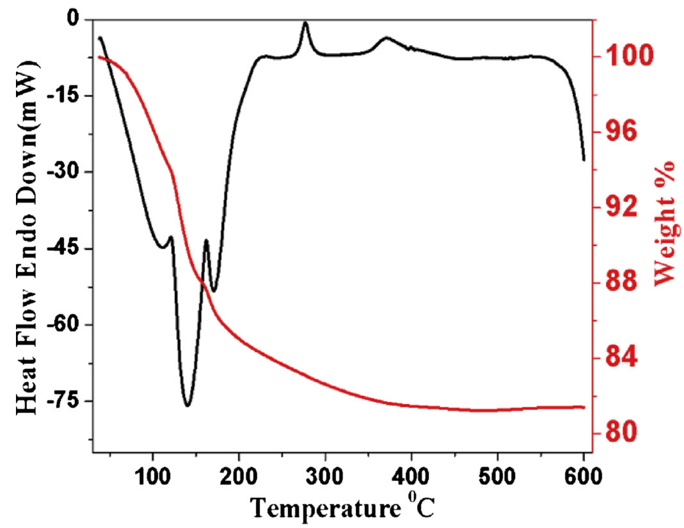

Fig. 2. TG-DTA plot of $60V_2O_5$–$5P_2O_5$–$35B_2O_3$ glass samples.

3.2. Thermal analysis

Fig. 2 shows thermal dehydration in $60V_2O_5$–$5P_2O_5$–$35B_2O_3$ samples. From TG, weight loss of 15% is in the temperature range of 30–200 °C which may be due to loss of water molecules. After this a steady loss in weight is observed till 300 °C, due to condensation of structural OH groups [3,10,11].

The DTA curve of 35 mol% of B_2O_3 glass sample consists of three endothermic peaks, which are attributed to the removal (evaporation) of water from the sample. A small endothermic change because of its second-order phase transition at around 230 °C may be assigned for the glass transition (Tg). The sharp exothermic peaks at around 275 °C may be due to the crystallization (Tc) of the glass [12,13].

At the same time the derivative of DTA (DDTA) is recorded and shown in Fig. 3. The temperature Tf_1 and Tf_2 endothermic and exothermic peaks can be exactly detected on DDTA curve from inflection points. The first-order reaction activation energy (E_a) is derived from Eq. (3) using Tf_1 and Tf_2 [3,7,14]. The endo-activation energy was found to be 17.3 ± 0.01 kJ/g-mol, whereas exo-activation energy was 55.1 ± 0.05 kJ/g-mol respectively, for 35 mol% of B_2O_3.

$$\frac{E_a}{R}\left(\frac{1}{Tf_1} - \frac{1}{Tf_2}\right) = 1.92 \quad (3)$$

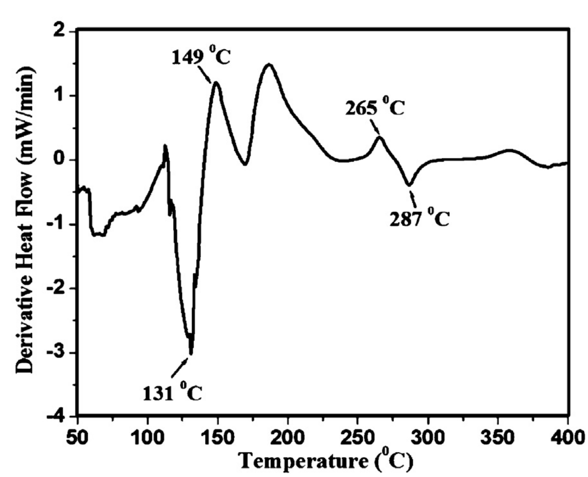

Fig. 3. Simultaneous recorded DDTA curve of $60V_2O_5$–$5P_2O_5$–$35B_2O_3$ glass samples.