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Effects of vitrification suppression on structure morphology, conductivity and dielectric properties of vanadium phosphate glasses

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Abstract

Vitrification suppression in the $(V_2O_5)_{1-x}$ $(P_2O_5)_x$ glasses where $x = 0.10$, 0.15, 0.20, and 0.25 was controlled by changing the rate of quenching glasses. The structure variations occurring in the glasses were detected by differential thermal analysis and optical microscope. The results implied the separation and growth of V_2O_5 orthorhombic microcrystal in the samples with $x = 0.10$ and 0.15 whereas other samples did not illustrate remarkable changes in their microstructure. However, in temperature range between 300 and 473 K a semiconducting behavior for all samples appears during the study of electrical conductivity-temperature dependence. A decrease in conductivity values accompanied with some variations in activation energies by reducing quenching rate was observed. The conductivity results suggested that the conduction occurs by the phonon assisted hopping of a small polaron between V^{4+} and V^{5+} states at relatively higher temperature range above $\theta_D/2$. Whereas at relatively low temperatures the conduction may occur by electron jumping between filled and empty states at Fermi level in the disordered matrix besides polaronic conduction. Reasonable values for the density of localized states, carrier concentration and carrier mobility were estimated and discussed. Also, dielectric constant and dielectric loss were studied as a function of frequency at different temperatures confirming the structure variations in the glass system.

Keywords: A. Glasses; B. Chemical synthesis; C. Thermogravimetric analysis (TGA)

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1. Introduction

Semiconducting glasses [1,2] have attracted a great attention because of their intriguing electrical properties and technological applications. Vanadium phosphate glasses have been considered to be of great interest because of their promising applications in the field of electronics [3–5]. The switching phenomenon in vanadium-based glasses attracts the attention of many investigators in the last decade [6–8]. The instability of the switching devices arises from the nucleation and the growth of microcrystalline phases after the long time aging under operation in the electronic circuits. The amorphous–crystalline transformation depends on both the annealing temperature at the vicinity of glass transition temperature and the time of annealing. Since this type of glass was found to be of strong resistance to transformation, a trial was done to suppress vitrification in the glass to obtain the desired microcrystalline phase by controlling the rate of quenching. Glasses containing transition metal ions with two valance states such as vanadium (V^{4+} or V^{5+}) in vanadium phosphate glasses results in localization of energy states within the energy gap width [9–11]. The empty energy state trap electrons (V^{4+}) may induce local deformation of the energy states (small polaron). Therefore, with the assistance of a phonon, the small polaron jumps to another empty state (V^{5+}) as its energy equal to the difference between the two states (V^{4+} and V^{5+}). The presence of the microcrystalline phase will alter the physical properties of vanadium phosphate glasses. The nucleation and growth of such microcrystallites in an amorphous matrix will cause a reduction the volume fraction of the amorphous portions in the glasses. Besides a change of bond satisfaction in the disordered system is also expected. These in turn may alter the electron

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localization in the amorphous system. Subsequently, the electrical conductivity may increase with increasing the volume fraction of the microcrystalline phase in vanadium-based glasses. The growth of such microcrystals may also increase the interfacial effects that lead to an increase of the dielectric constants of glasses.

The present work aims to suppress vitrification of vanadium phosphate glasses in order to create microcrystalline phases in the glasses. A correlation between the separation of microcrystals in the amorphous matrix and both conductivity and dielectric properties is our main target.

2. Experimental

Vanadium phosphate glasses $(V_2O_5)_{1-x}(P_2O_5)_x$ where $x = 0.10$, 0.15, 0.20, and 0.25 were prepared from melt of oxides mixture of V_2O_5 and P_2O_5 (reagent grade). The oxides mixture was firstly reacted at 613 K for one hour to minimize the volatilization of P_2O_5. Then the temperature was raised gradually to 1123 K in order to complete the reaction in a period of five hours. The melt was shacked several times to enhance both reaction and homogeneity. After synthesis the melt was poured onto a steel plate kept at the desired temperature (303, 453 or 673 K) and left to cool down slowly to room temperature. The obtained samples were kept in a discicator over P_2O_5 at room temperature to isolate them from moisture. Differential thermal analysis (DTA) was carried out for all glasses on Schimadzu instrument (model Dt 30) using a heating rate of 20 K/min, 10 mg of sample in the temperature range 293–773 K with α-Al_2O_3 as the inert reference material. The samples were prepared for the optical microscope investigations by polishing their surface by several stages coarse, medium and fine until the surface became free from any scratches. The sample surface scanned and the area of interest was photographed automatically under the required magnification by using a Nikkon optical microscope provided with camera. The dielectric properties of glasses were measured using a programmable automatic RLC Phillips bridge (PM 6304 type). The d.c. conductivity was measured using a Keithely 610 C electrometer. The ohmic behavior was ascertained from the linearity of I–V characteristics.

3. Results and discussion

3.1. Structural transformation in vanadium phosphate glasses

3.1.1. Differential thermal analysis

The structural transformations in vanadium phosphate glasses are detected out using the DTA technique and morphology. For DTA, six samples which cast at temperatures (303, 453 and 673 K) are studied, three with $x = 0.10$, and the other with $x = 0.25$. Fig. 1 illustrates DTA thermograms for (i) $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ and (ii) $(V_2O_5)_{0.90}(P_2O_5)_{0.10}$ glass samples cast at (a) 303 K, (b) 453 K and (c) 673 K. The following results are obtained from this Figure: (i) For each cast glass at lower temperature, 303 K, exothermic peaks appear which attributed to crystallization process are started, Fig. 1(ii-a). (ii) The DTA thermograms for each sample cast at higher temperature 453 or 673 K with $x = 0.25$ showed broad and depressive exothermic peak. The observed broad hump beyond the T_c for $x = 0.25$, Fig. 1(i), may be attributed to amorphous–amorphous transition. (iii) The further increase of casting temperature, 673 K, for $x = 0.25$, a pronounced peak was observed, Fig. 1(i-c). (iv) For each sample with $x = 0.10$ the peak of crystallization process becomes smaller and shifts to higher temperature with decreasing the quenching rate (i.e. raising the casting temperature). This confirms our expectation of increasing the possibility of nucleation and growth of microcrystals with decreasing quenching rate. However, the massive separation of crystalline phase leads to weakness or disappearance of the

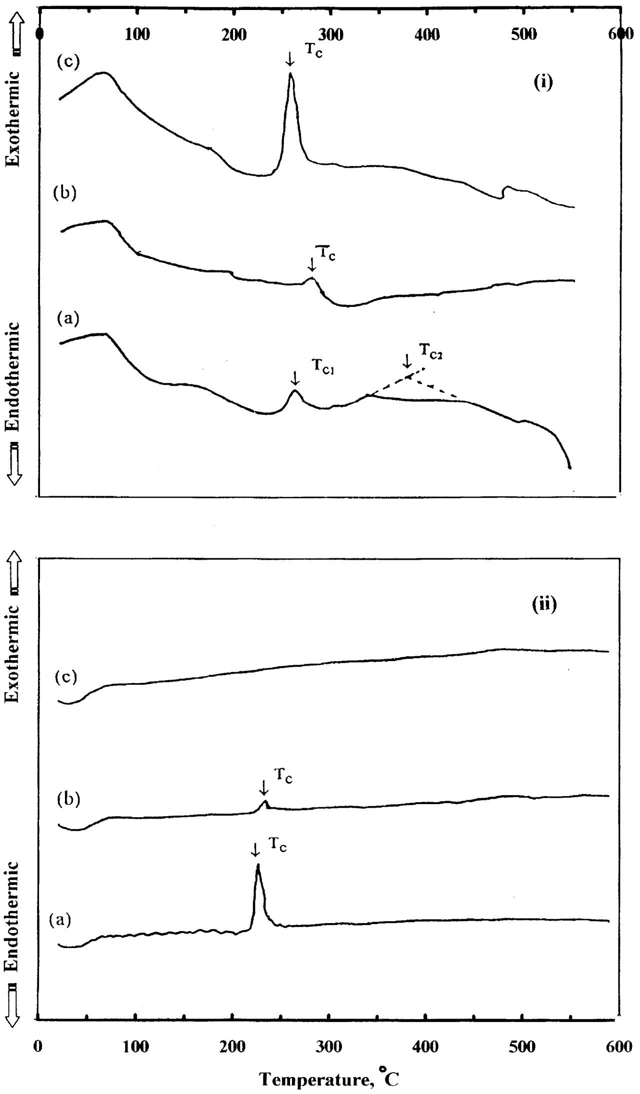

Fig. 1. DTA thermograms for (i) $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ and (ii) $(V_2O_5)_{0.90}(P_2O_5)_{0.10}$ glasses cast at (a) 303 K, (b) 453 K and (c) 673 K.

exothermic peaks attributed to crystallization process as shown in our case, Fig. 1(ii).

3.1.2. Morphology of vanadium phosphate glasses

The morphology of $(V_2O_5)_{0.90}(P_2O_5)_{0.10}$ glasses were examined for glass samples cast at different temperatures, 303, 453, 673 K, Fig. 2(a). In general, at the lowest casting temperature 303 K the microstructure of the present sample shows a start of nucleation. With increasing casting temperature to 453 K, the growth of microcrystals could be observed. The further raising of the casting temperature to 673 K leads to higher degree of crystallization. The micrograph in Fig. 2(a) for casting temperature equal 673 K illustrates the diffusion fields of adjacent particles and the regime of the overlapping. The obtained microstructure confirms the result of X-ray diffraction of these glass samples [12]. To pointed out the effect of vanadium oxide concentration on the structure transformation in vanadium phosphate glasses, the morphology of $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ sample cast at 303 K is studied (Fig. 2(b)). The higher V_2O_5 concentration sample ($x = 0.10$, cast at 303 K) shows a higher degree in crystallization than the sample presented in Fig. 2(b). The observation of this massive crystallinity with increasing the concentration of the V_2O_5 shows that the increase of crystallinity in good agreement with the separation of V_2O_5 from the amorphous matrix. Glasses crystallize by nucleation and growth process. Growth may be primary, eutectic or polymorphic. Primary crystallization is generally controlled by diffusion. If we assume that the diffusion rate D is independent of the concentration, the radius r of a spherical crystallizing particle will be proportional to the time t as, $r \sim \delta(Dt)^{1/2}$, where the growth rate dG/dt is given by $dG/dt \sim 1/2\delta^2 Dr^{-1}$, where δ is a dimensionless parameter from the composition at interface between the particle and the amorphous matrix. The previous study showed that if the casting temperature was higher than T_g, the volume density of the crystals in fully crystallized glasses increased by orders of magnitude due probably to homogenous nucleation [13]. This was observed in all metal-metalloid glasses for the polymorphic as well

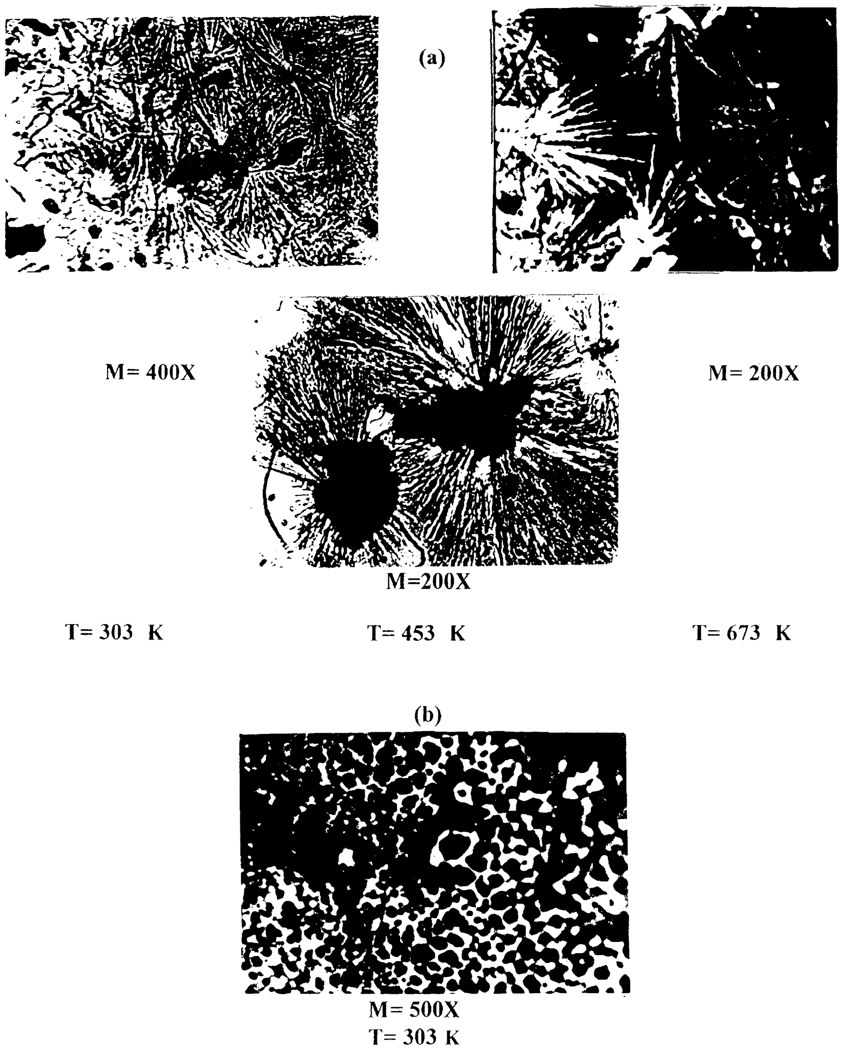

Fig. 2. (a) The morphology of $(V_2O_5)_{0.90}(P_2O_5)_{0.10}$ glasses for samples cast at different temperatures, 303, 453 and 673 K. (b) The morphology of $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ glass sample cast at 303 K.

as for the eutectic crystallization reactions and to less extent for primary crystallization.

3.2. Temperature dependence of d.c. conductivity

The effect of casting temperature on the electrical conductivity of the vanadium phosphate glasses having different compositions [$x = 0.10$, 0.15, 0.20 and 0.25] has been studied in the temperature range 303–473 K. Fig. 3, as a representative diagram, illustrates the temperature dependence of the d.c. conductivity, σ, for the $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ glass cast at different temperatures. Semilogarithmic plots of σT versus $10^3/T$ illustrate rectilinear lines for glasses under investigation. However, the electrical conductivity, σ, in transition metal oxide based glasses could be discussed on the basis of Mott and Davis relation [14,5],

$$\sigma \cong c(1 - c)^{s+1}/kT \exp(-2\alpha R)\exp(-W/kT) \qquad (1)$$

where c is the fraction of sites occupied by an electron (V^{4+}) of low oxidation state, (1-c) represents the empty sites fraction (V^{5+}), s is the average number of empty sites on coordinated sphere, k is Boltzmann's constant, T is the absolute temperature, α is the decay factor of the electron wave function, R is the inter spacing distance between filled and empty sites and W is the activation energy for conduction. The two regions in $\sigma T - 10^3/T$ relation describe the conduction process in vanadium phosphate glasses at relatively low and high temperature ranges. The values of the activation energies W_1, W_2 for both regions were obtained and listed in Table 1. The values of the activation energy in the first region, W_1, lie in the range 0.21–0.39 eV whereas W_2 of the second region lie in the range 0.34–0.56 eV. The values of W_2 decrease regularly with increasing vanadium content (samples cast at the lowest temperature 303 K) in agreement with those obtained by several investigators [5–8]. In addition the variation in the values of activation energies of both regions of conduction does not show regular change with varying quenching rates and/or vanadium contents in vanadium phosphate glasses that can be attributed to the phase separation and subsequently the formation of domain interfaces.

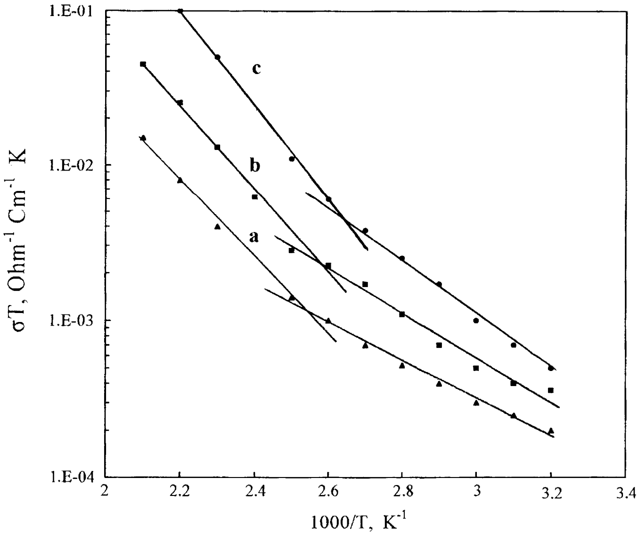

Fig. 3. Semilogarithmic plots of σT versus $10^3/T$ for $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ glasses cast at different temperatures (a: 303 K, b: 453 K and c: 673 K).

Table 1
The values of θ_D (K) and $\nu_{ph} \times 10^{-13}$ (Hz), W_1 and W_2 (ev) for $(V_2O_5)_{1-x}(P_2O_5)_x$ glasses cast at different temperatures

Casting temperature (K)	x	θ_D	ν_{ph}	W_1	W_2
303	0.25	914	1.71	0.25	0.56
	0.20	1054	1.67	0.25	0.49
	0.15	1000	1.61	0.21	0.47
	0.10	904	1.51	0.23	0.40
453	0.25	1054	1.67	0.25	0.56
	0.20	860	1.47	0.22	0.46
	0.15	451.6	1.51	0.27	0.37
	0.10	1178	1.8	0.3	0.47
673	0.25	1068	1.68	0.39	0.78
	0.20	852	1.46	0.36	0.55
	0.15	946	1.55	0.29	0.34
	0.10	884	1.5	0.24	0.37

It is found that the d.c. conductivity increases with increasing V_2O_5 content and/or the casting temperature, obeying the following empirical relation,

$$\sigma = A \exp(F/F_0) \qquad (2)$$

where A is a pre-exponential factor refers to the conductivity of isolated vanadium ions in the glass network, F is the mole fraction percent of V_2O_5, and F_0 is a characteristic concentration of V_2O_5 which may depend on: (i) the concentration of formed microcrystalline phase of V_2O_5, the ratio of V^{+4}/V in vanadium phosphate glasses and (ii) the interfaces of the different phases (amorphous–amorphous, amorphous–crystalline and crystalline–crystalline). The values of A and F_0, which fit relation (2) are obtained and listed in Table 2. The obtained data show that the value of F_0 decreases as the casting temperature is raised from 303 to 453 or 453 or 673 K, which may refer to a change of V^{4+} coordination.

Table 2
The fitting parameters A (Ω/cm) and F_0 deduced at different ambient temperatures for vanadium phosphate glasses cast at different temperatures

Casting temperature (K)	T (K)	A	F_0
303	313	5.91×10^{-14}	4.70
	373	9.61×10^{-14}	4.51
	423	4.41×10^{-14}	4.05
453	313	2.46×10^{-15}	3.78
	373	1.52×10^{-15}	3.48
	423	1.23×10^{-13}	3.98
673	313	2.05×10^{-20}	2.37
	373	2.25×10^{-18}	2.59
	423	2.13×10^{-15}	3.11

The amorphous semiconductors are characterized, in general, by the thermal activation of their conduction in wide range of temperature. The d.c. conductivity temperature dependence models could be summarized as follows [14]: (a) in the low temperature range conductivity domains by charge carrier tunneling or hopping between field and empty states at the fermi level (b) in the moderate temperature range, the conduction arises by charge carrier excitation into the localized states at the band edge and (c) in the relatively high temperature range conduction occurs by the charge carriers excitation beyond the mobility shoulders into excited states where the activation energy is temperature dependent.

In transition metal oxide based glasses conduction dominates by electronic transfer (small polaron) between ions of different valences, such as V^{4+} and V^{5+} in the present samples [8,15]. According to relation (1), the jumping rate of polaron between ions depends on the jumping distance, R, and the energy difference of electron located at different sites due to local variations in glass matrix, oxygen coordination or the distribution of charged impurity atoms. According to Hench [16], conduction band in V_2O_5 based materials, formed on electronic orbitals of V^{5+} ions while electrons associated with V^{4+} are considered to be polarons and having lower energy by an amount proportional to the polaron binding energy. The localization of energy levels is completed at sufficient distortion of atomic arrangement in the material. These levels will be the localized polaron state.

The casting of vanadium phosphate melts at room temperature, may result in the formation of short range ordered regions, which depend on the vanadium phosphate composition. By increasing vanadium content in the glasses (over a critical concentration at which solid solution is formed) the possibility of nucleation and growth of such short range ordered regions might increase as the casting temperature is increased. The further increase of casting temperature means the decreasing of quenching rate and hence the short range ordered regions in the amorphous matrix have a chance to grow. Therefore, the volume fraction of crystalline phases will control the conductivity values in vanadium phosphate glasses. The volume fraction of induced conducting regions will also grow with increasing vanadium concentration in the glasses at the same casting temperature due to the extensive separation of V_2O_5. Some changes in the ratio of V^{+4}/V are expected as a result of the changing preparation conditions [17].

The activation energy W in Eq. (1) has been considered as a summation of two terms [14],

$$W = W_H + W_D \tag{3}$$

where W_H is the hopping energy, W_D is the disorder energy that is dominating below $\theta_D/4$; θ_D being the Debye's temperature. The observed kink in $\sigma T - 10^3/T$ relation for the different compositions of $(V_2O_5)_{1-x}(P_2O_5)_x$ at different casting temperatures predict a transition temperature, $T_x(\cong \theta_D/2)$, at which the conduction mechanism may change. The values of θ_D are obtained and listed also in Table 1. They are in satisfactory agreement with the IR absorption band at 380 cm^{-1} belonging to vanadium rich glasses [5]. Thus the thermal energy $k\theta_D$ is equal to the expected phonon energy $h\nu_{ph}$ of dominated phonon mode. The values of phonon frequencies ν_{ph} were calculated and listed in Table 1. The region below the kink lies between $\theta_D/4$ and $\theta_D/2$ suggests a transition region of conduction between low and high temperatures. This led us to discuss the temperature dependence of conductivity according to the variable range hopping in amorphous solids [9],

$$\sigma T = \sigma_0 \exp(-T_0/T)^{1/4} \tag{4}$$

where σ_0 is the pre-exponential parameter, $T_0 = 12.5\alpha^3/N(E_f)k$, and $N(E_f)$ is the density of localized states at Fermi level. Semilogarithmic plot of σT versus $T^{-1/4}$ shows straight lines, Fig. 4. By assuming that $1/\alpha = 10$ Å, the values of $N(E_f)$ are deduced and presented in Table 3. It is clear that the values of $N_2(E_f)$ (at higher temperature) are smaller than $N_1(E_f)$ (at lower temperatures) indicating that conduction at relatively low temperature range occurs by the electron jumping to the empty of defects in the disordered matrix besides the contribution of polarons.

Mott and Davis have summarized an approach of the existence of polarons in transition metal oxide based glasses [14]. They analyzed the polarization well into normal modes of the lattice vibration gives the reduced ion separation distance rather than polaron radius,

$$r = \frac{1}{2}(\pi/6N)^{1/3} \tag{5}$$

where N is the concentration of potential wells for electrons. The localized states have considered here to be equivalent to these wells. However the average separation distance of these wells (the reduced vanadium atom separation distance) are obtained for glasses under investigation and

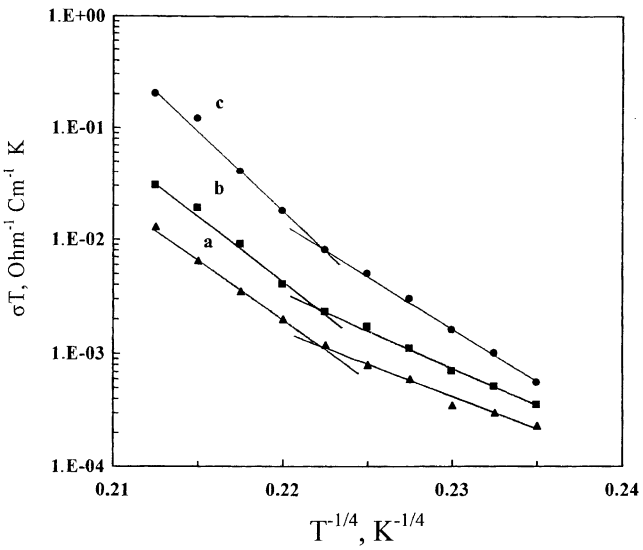

Fig. 4. Semilogarithmic plots of σT versus $T^{1/4}$ for $(V_2O_5)_{0.75}(P_2O_5)_{0.25}$ glasses cast at different temperatures (a: 303 K, b: 453 K and c: 673 K).

Table 3
The deduced values of the density of localized states $N_1(E_f)$, $N_2(E_f)$ (cm^{-3}/ev), the values of carrier concentration n_1, n_2 (cm^{-3}), the values of carrier mobility μ_1, μ_2 (cm^2/(v s)) and the separation distance of reduced ions r_1, r_2 (Å) in $(V_2O_5)_{1-x}(P_2O_5)_x$ glasses

Cast temperature (K)	x	$N_1(E_f) \times 10^{20}$	$n_1 \times 10^{18}$	$\mu_1 \times 10^6$	r_1	$N_2(E_f) \times 10^{19}$	$n_2 \times 10^{18}$	$\mu_2 \times 10^3$	r_2
303	0.25	3.65	9.80	0.37	5.64	3.32	1.35	0.14	12.54
	0.20	2.97	8.00	1.09	6.04	3.93	1.61	0.25	11.86
	0.15	3.84	10.3	2.00	5.55	4.25	1.74	0.58	11.55
	0.10	2.64	7.10	13.9	6.28	8.06	3.3	1.24	9.33
453	0.25	3.71	1.00	7.80	5.61	3.54	0.41	0.29	12.27
	0.20	2.40	6.46	2.44	6.49	5.33	2.18	0.58	10.71
	0.15	1.34	3.60	39.0	7.88	–	–	–	–
	0.10	1.65	4.40	97.0	7.35	–	–	–	–
673	0.25	0.69	1.85	5.40	9.82	0.91	0.37	1.78	19.30
	0.20	0.56	1.50	14.1	10.5	2.47	1.01	0.17	13.84
	0.15	1.77	4.76	255	7.18	–	–	–	–
	0.10	1.26	3.40	880	8.04	–	–	–	–

listed in Table 3. It is clear that the values of r_1 (at lower temperature range) are higher than r_2 (at higher temperature range). The values of r_1 are in satisfactory agreement with those obtained by Sayer and Mansingh [5].

The values of the density of localized states $N(E_f)$ at Fermi level led us to estimate the concentration of localized electrons contributing in conduction process, $n = N(E_f)kT$. Table 3 illustrates the deduced values of n at 313 and 473 K which lie in the range 3.7×10^{17}–1.03×10^{19} cm^{-3}. Similar values are obtained by Bahri et al. [18] during studying the effect of additives on the electrical properties of P_2O_5–Fe_2O_3 glasses. By using the values of the electrical conductivity at 313 and 473 K, the values of charge carrier drift mobility were estimated ($\sigma = qn\mu$) for samples under investigation and given in Table 3. It is concluded that, the drift mobility increases when the casting temperature and/or vanadium content is increased. In addition to that the drift mobility lies in the range (3.7×10^{-7}–1.78×10^{-3} cm^2/(V s)), which predicts the hopping conduction. It has been proposed a relation to explain the drift mobility in non-adiabatic system in transition metal oxide based glasses [14],

$$\mu = \frac{3}{2}(eR^2J^2)(\pi/kTW_h)^{1/2}\exp(-W_h/kT) \tag{6}$$

where $J = e^{-\alpha R}$ is the polaron band width related to the electron wave function overlap on adjacent sites and W_h is the hopping energy. This relation predicts that the conductivity temperature is due to the thermal activation of drift mobility rather than concentration of charge carriers. The obtained values of drift mobility at 473 K are higher than the drift mobility at 313 K which goes in parallel way with relation (1).

3.3. Dielectric properties of $(V_2O_5)_{1-x}$ $(P_2O_5)_x$ glasses

In this section both real and imaginary components of the dielectric constant ϵ' and dielectric loss ϵ'' were studied as a function of frequency in the temperature range 303–473 K for $(V_2O_5)_{1-x}$ $(P_2O_5)_x$ glasses, Figs. 5 and 6 illustrate the general behaviors of both ϵ' and ϵ'' against frequency for two vanadium phosphate glass samples cast at 303 K, as representative diagrams. It is clear from Fig. 5 that the dielectric response (the decrease of ϵ' with frequency) can be divided into two regions, the first of low responsibility at low frequency range, while the second region shows a strong frequency dependence appearing at relatively higher frequencies. The ϵ'–f behavior shifts towards higher frequency range with increasing ambient temperature. On the other hand, the ϵ''–f behavior shows a decrease in ϵ'' with increasing frequency for all glasses under investigation, Fig. 6. For vanadium phosphate glasses, Mansingh et al. [19] showed a dielectric loss peak characterizing dielectric relaxation appeared at low temperature range

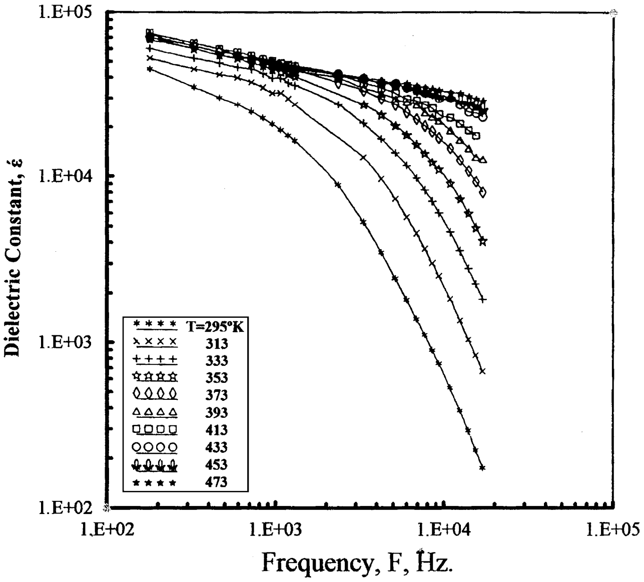

Fig. 5. Frequency dependence of the dielectric constant ϵ' at different temperatures for a $(V_2O_5)_{0.80}(P_2O_5)_{0.20}$ glass cast at 303 K.

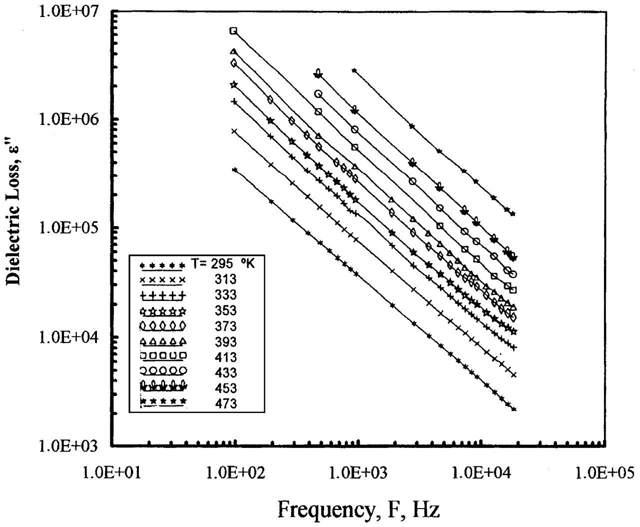

Fig. 6. Frequency dependence of the dielectric loss ϵ'' at different temperatures for a $(V_2O_5)_{0.85}(P_2O_5)_{0.15}$ glass cast at 303 K.

77–300 K. This peak was not observed in our samples, which were tested at higher temperature range. By assuming a symmetric distribution of relaxation time, both the dielectric constant ϵ' and loss $\in''$ can be described by the following relations [20–22],

$$\epsilon''/(\epsilon_0 - \epsilon_\infty) = \{(\omega\tau)^{1-g}\cos(g\pi/2)[\epsilon_0 - \epsilon_\infty]\}/\{1 + 2(g\tau)^{1-g}\sin(g\pi/2) + (\omega\tau)^{2(1-g)}\} \qquad (7)$$

$$(\epsilon' - \epsilon_0)/(\epsilon_0 - \epsilon_\infty) = \{1 + (\omega\tau)^{1-g}\sin(g\pi/2)\}/\{1 + 2(\omega\tau)^{1-g}\sin(g\pi/2) + (\omega\tau)^{2(1-g)}\} \qquad (8)$$

where τ is the relaxation time, ϵ_0 and ϵ_∞ is the dielectric constants at low ($\omega \ll 1/\tau$) and infinite ($\omega \gg 1/\tau$) frequencies respectively and g is a distribution parameter with values between 0 and 1. Relations (7) and (8) tend to satisfy Debye equations for single relaxation when $g = 0$.

According to Jonscher [21] the obtained behavior of both dielectric constants ϵ' and losses ϵ'', Figs. 5 and 6 can be explained as follows. The dielectric response usually starts, in semiconducting material, as the applied field frequency keeps away from the domination of d.c. conductivity ($\omega \gg 1$). In addition, the domain interfaces may play a significant role in controlling the dielectric relaxation in our glass samples. The dielectric response of the space charge at domain interfaces is determined by: (i) the free carrier densities at the space charge edge, this takes place with a time constant given by the space charge relaxation time, (ii) the dielectric response properties of the lattice itself, this is dominated by atomic and ionic relaxations, (iii) the response of the generation–recombination process, determined by the carrier life time, and (iv) the response of trapping effects from which electrons are trapped at deep traps with mean trapping times much longer than the average recombination times Thus the observed shift of dielectric behavior, Fig. 5, towards higher frequency range with raising temperature can be attributed to the enhancement of d.c. conductivity which reduces the dielectric response. The dielectric response, in general, can be interpreted by assuming the equivalent circuit shown in Fig. 7(a). The diagram represents the behavior of a series combination of one universal capacitor C_i, corresponds to a barrier at domain interfaces, and a parallel combination of universal capacitor C_{B1} with a parallel conductance G_{B1} representing the bulk of the sample. It notes that at much closer to d.c., the response dominated by the barrier capacitor. When the frequency was increased (strong dependence region), Fig. 5, the bulk resistor $1/G_{B1}$ with C_{B1} dominates.

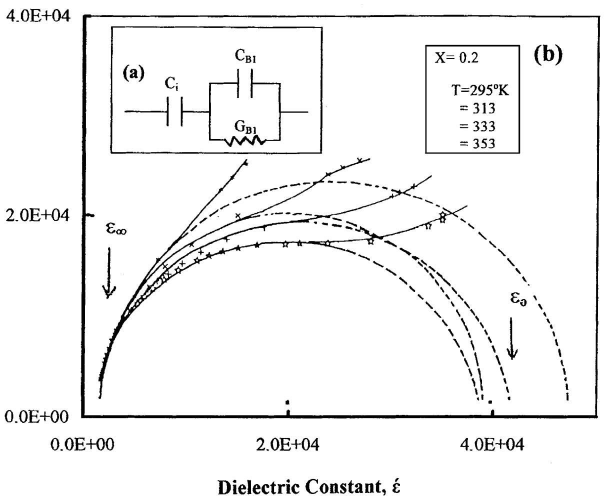

Fig. 7. (a) The equivalent circuit and (b) semicircle plots of ϵ'' versus ϵ' for $(V_2O_5)_{0.80}(P_2V_5)_{0.20}$ glasses cast at 303 K.

In this type of glasses, the previous investigation [19] showed that Debye's relaxation dominated in the temperature range 77–300 K. However, in the present work we will try to obtain some information about the relaxation process in the higher temperature range 300–473 K. The plot of complex permittivity (ϵ'' versus ϵ') illustrates an arc (semicircle) intersecting ϵ' axis at ϵ_0 and ϵ_∞, the static and the infinite dielectric constants respectively, Fig. 7(b). Sayer and Mansingh [5] have discussed the variation of dielectric properties in transition metal based glasses on the basis of electron jumping between the lower valance ions

Table 4
The values of W_D, W_τ (eV) and τ_0 (s) for $(V_2O_5)_{1-x}(P_2O_5)_x$ glasses cast at different temperatures

Cast temperature (K)	x	W_D	τ_0	W_τ
303	0.25	0.25	1.2×10^{-11}	0.44
673	0.25	0.12	1.02×10^{-7}	0.19
303	0.20	0.11	6.2×10^{-9}	0.26
453	0.20	0.35	4.4×10^{-13}	0.53

Table 5
The hopping energy W_m (eV) for $(V_2O_5)_{1-x}(P_2O_5)_x$ glasses cast at different temperatures

Cast temperature (K)	x	295	313	333	353	373	393	413	433	453	473
303	0.25	0.11	0.12	0.19	0.31	0.23	0.23	0.21	0.19	0.18	0.20
	0.20	0.12	0.14	0.19	0.28	0.44	0.23	0.21	0.20	–	0.19
	0.15	0.12	0.12	0.13	0.13	0.14	0.14	0.16	0.15	0.16	0.17
	0.10	0.11	0.12	0.14	0.20	0.16	0.17	0.16	0.19	0.18	0.19
453	0.25	–	0.11	0.15	0.20	0.38	0.32	0.26	0.23	0.22	0.21
	0.20	0.18	0.14	0.19	0.27	0.15	0.20	0.19	0.19	0.19	0.19
	0.15	0.11	0.11	0.13	0.14	0.14	0.15	0.15	0.15	0.16	0.17
	0.10	0.10	0.11	0.12	0.12	0.13	–	–	–	–	–
673	0.25	0.11	0.12	0.14	0.16	0.21	0.25	0.22	0.20	0.20	0.19
	0.20	0.11	0.12	0.14	0.16	0.16	0.19	0.20	0.15	0.16	0.20
	0.15	0.11	0.11	0.12	0.12	0.14	0.14	0.15	0.16	0.16	0.17
	0.10	0.10	0.11	0.12	0.12	0.13	0.14	0.14	0.15	–	–

and that of higher valance. According to their studies the characteristic value of dielectric constant ($\epsilon_s - \epsilon_\infty$) could be represented by the following relation,

$$\epsilon_s - \epsilon_\infty = 4/3\pi(Ne^2R^2/kT)C(1-C)\exp(-W_D/kT) \qquad (9)$$

The values of activation energy W_D were obtained. By using the least square fitting of relation (9) and listed in Table 4. It is clear that the values of W_D are almost lower than the values of the activation energy obtained from conductivity-temperature dependence. This could be attributed to the contribution of interfacial polarization besides the electronic one (low frequency range). Subsequently, the dielectric relaxation times were obtained at $\omega\tau \sim 1$ at different ambient temperatures for vanadium phosphate glasses under investigation. It is found that, τ decreases with increasing temperature obeying the following Arrhenius relation,

$$\tau \approx \tau_0 \exp(W_\tau/kT) \qquad (10)$$

where W_τ is an activation energy of relaxation in vanadium phosphate glasses and τ_0 is the relaxation time at $T = \infty$. The values of W_τ and τ_0 are obtained by using the least square fitting of relation (10) and listed in Table 4. The values of W_τ are in satisfactory agreement with those of W_2 (d.c. conductivity measurements), which predicts that the same mechanism governs both the d.c. conductivity and relaxation process.

Guintini et al. [23] assumed a distribution of the relaxation time and they derived a relation describing the frequency dependence of the dielectric loss in amorphous solids,

$$\epsilon''(\omega) = (\epsilon_0 - \epsilon_\infty)2\pi^2 N(\mathrm{n}e^2/\epsilon_0)^3 kT\tau_0^m W_m^{-4}\omega^{-m} \qquad (11)$$

where N is the concentration of localized states, n is the number of electrons that hop, W_m is the energy required to move an electron from one site to infinite and $m = -4kT/W_m$. The logarithmic plots of ϵ'' versus frequency for each one of the investigated samples shows straight line, typical plots shown in Fig. 6 as a representative diagram, satisfying relation (11). According to this model the values of W_m are obtained and listed in Table 5. From this Table one notices that W_m values are lower than the activation the activation energies obtained from temperature dependence of conductivity. This could be attributed to the unsuccessful hopping between filled and empty localized states at Fermi level [24] besides polaron hopping between V^{4+} and V^{5+} sites. On the other hand, the values of W_m estimated using the data of Guintini et al. [23] for chalcogenide glasses are higher than our present data which can be attributed to the significant contribution of polarons besides localized electrons in polarization in transition metal based glasses.

4. Conclusions

From the obtained results and discussion one can conclude the following:

1. The decrease of the quenching rate and/or the vanadium content enhance the separation and growth of V_2O_5 microcrystals in vanadium phosphate glasses.
2. The increase of the degree of crystallinity and/or vanadium content enhance the electrical conductivity in vanadium phosphate glasses.
3. The glass domain interfaces (amorphous–amorphous and amorphous–crystal interfaces) play an important role in both conduction and dielectric properties of vanadium phosphate glasses.

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