

DTA and annealing investigations of some V_2O_5/P_2O_5 glasses

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Received 19 December 1995, accepted 16 May 1996

Abstract : DTA thermograms were recorded for some V_2O_5/P_2O_5 glasses with different composition (9.33, 18, 29, 53, 33 and 65 mole% of V_2O_5) in the temperature range from 27 to 650°C. Two exothermic peaks were observed and referred to relaxation and crystallization processes in order of increasing temperature respectively. In addition to the above two peaks, an endothermic peak was observed between them and attributed to the glass transition of each sample. Also the effects of the heating rate as well as the annealing time on the observed peaks (relaxation and ordering) were investigated, where the activation energy of crystallization E_c was calculated according to Kissinger and Ozawa models. The dependences of both E_c and glass transition temperature T_g on glass composition were also investigated.

Keywords : Vanadate phosphate glasses, phase transformation and annealing

PACS Nos. : 8130, 8140E and 8140G

1. Introduction

It is known that alkali metavanadate crystals have a chain structure composed of the VO_4 tetrahedra and these VO_4 tetrahedra were found in the skeleton of metavanadate glass [1]. Structure studies of the V_2O_5 crystal [2,3] revealed that each V^{5+} ion is making a distorted VO_5 tetragonal pyramid, which can also be viewed as a distorted VO_5 trigonal bipyramid, sharing edges and corners to form a layer structure. The coordination number of the V^{5+} ion is always 5 in the case of the V_2O_5/P_2O_5 glasses and they are composed of the interconnected and distorted VO_5 tetragonal pyramids [4]. Also, structural studies of vanadate glasses containing Fe_2O_3 in the V_2O_5 matrix [5] showed that the Fe^{3+} ions occupy substitutional position in all glass composition without affecting the V=O bond vibration.

DTA thermograms of the V_2O_5/P_2O_5 glasses containing 5 mol% Fe_2O_3 as reported [6] consist of an endothermic peak due to glass transition and one or a few exothermic peak (s) due to crystallization. The same authors reported also that the distinct increase in the

glass transition temperature T_g of the V_2O_5/P_2O_5 glasses, observed with increasing the P_2O_5 content, is ascribed to a continuous change of the glass matrix having a layer structure composed of the VO_5 tetragonal pyramids into a more complicated three dimensional structure composed of the VO_5 tetrahedra.

Since the glass transition reflects a change in the coordination number of the network forming atoms and a destruction of the network structure brought about by the formation of some non-bridging atoms, DTA studies on the structure of several glasses were performed and revealed that T_g is closely correlated with the change in the coordination number of glass forming atoms (network former) and with the formation of nonbridging oxygen [7-14], fluorine [15] and chlorine atoms [16]. A formation of non-bridging oxygen, fluorine and chlorine atoms in the glass is equivalent to devitrification of the glass matrix.

In the present work, it is aimed to investigate the phase transformations of some V_2O_5/P_2O_5 glasses and the effect of annealing on these transitions.

2. Experimental technique

Vanadium phosphate glasses of starting compositions expressed in mole%, were prepared by melt-quench technique. The final product are chemically analysed and these techniques are explained in details, previously [17]. A micro differential analyser (Shemadzu-DT 30) was used for studying the changes in the state of the glass sample during heating. The glass sample of constant mass and a thermally stable reference material (Al_2O_3) were put side by side in the furnace. The temperature variation $\Delta T^\circ C$ between the sample and the reference material, in addition to the temperature of the oven, were recorded simultaneously.

DTA runs were carried out from $27^\circ C$ up to $650^\circ C$, at different heating rates, 10, 15, 20 and $30^\circ C/min$, noting that at each heating rate, the temperature difference ΔT between the tested glass and the reference specimen is detected, amplified and recorded to be a peak or a valley.

3. Results and discussion

3.1. Effect of heating rate on DTA thermograms of V_2O_5/P_2O_5 glasses :

The dependence of the DTA thermograms on the heating rate for some prepared V_2O_5/P_2O_5 glasses with different compositions, 18, 29, 53, 33 and 65 mol% of V_2O_5 is investigated and shown in Figures (1a, b, c and d) respectively. The measurements of the tested specimen were carried out in the temperature range from 27 to $650^\circ C$ at different heating rates, 10, 15, 20 and $30^\circ C/min$. In general, each DTA curve in this figure, reveals two exothermic peaks and an endothermic one between them. However, on the plots corresponding to the sample with 29 mol% of V_2O_5 , there is one more exothermic peak. The first exothermic peak observed in DTA thermograms may be due to relaxation [18]. The other exothermic peak(s) is/are due to crystallization as a result of the formation of some ordered regions upon heating the glass. The last one which occurred between the above peaks is the

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endothermic peak, attributed to glass transition. The DTA thermograms have been used to study the amorphous crystalline-transformation in chalcogenide glasses. This has been done by deducing the order of reaction n and the apparent activation energy of the partial crystallization or ordering E_c [19]. The values of n were determined using the shape index

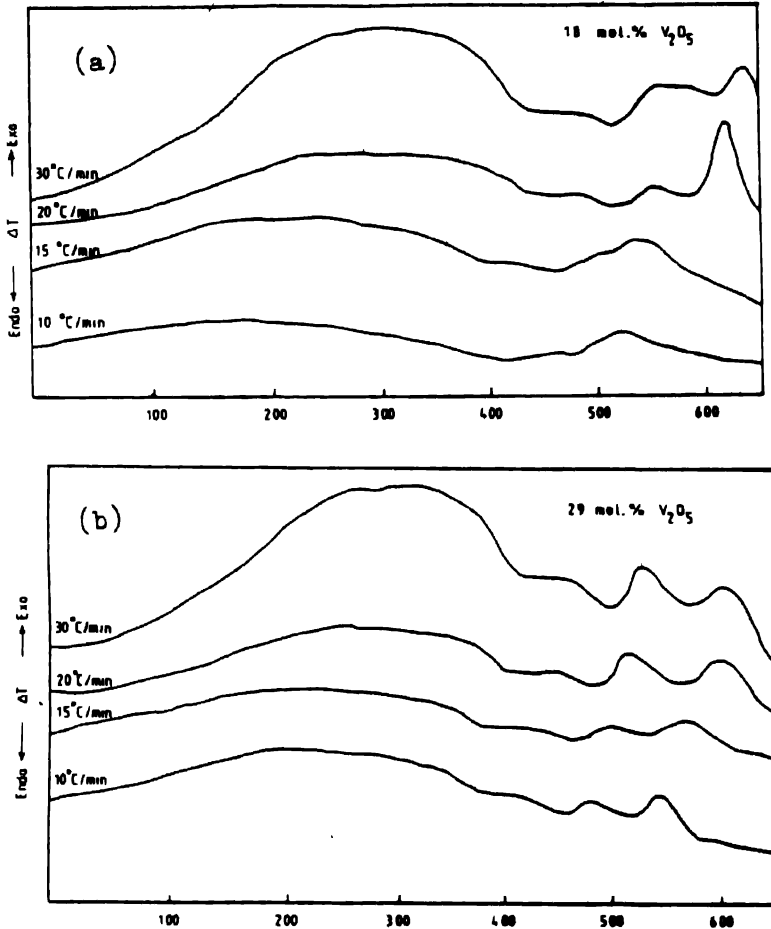


Figure 1. The effect of heating rate on the DTA thermograms of the V_2O_5/P_2O_5 glasses.

method [20], which reports that $n = 1.26 \sqrt{s}$ where s is the ratio of the base parts of the peak on the base line of DTA thermogram. And the values of E_c could be determined by using any of the following equations (1) and/or (2) which were suggested by Kissinger [20] and Ozawa [21] respectively.

$$\ln(T_c^2/\phi) = (E_c/RT_c) + \text{constant}, \quad (1)$$

$$\ln(\phi) = -(E_c/RT_c) + \text{constant}, \quad (2)$$

where ϕ is the heating rate, T_c is the crystallization temperature and R is the universal gas constant. These equations are plotted for all investigated glasses and shown in Figures (2a

and b). The calculated values for the activation energy of crystallization (ordering) and the order of reaction n are illustrated in Table 1

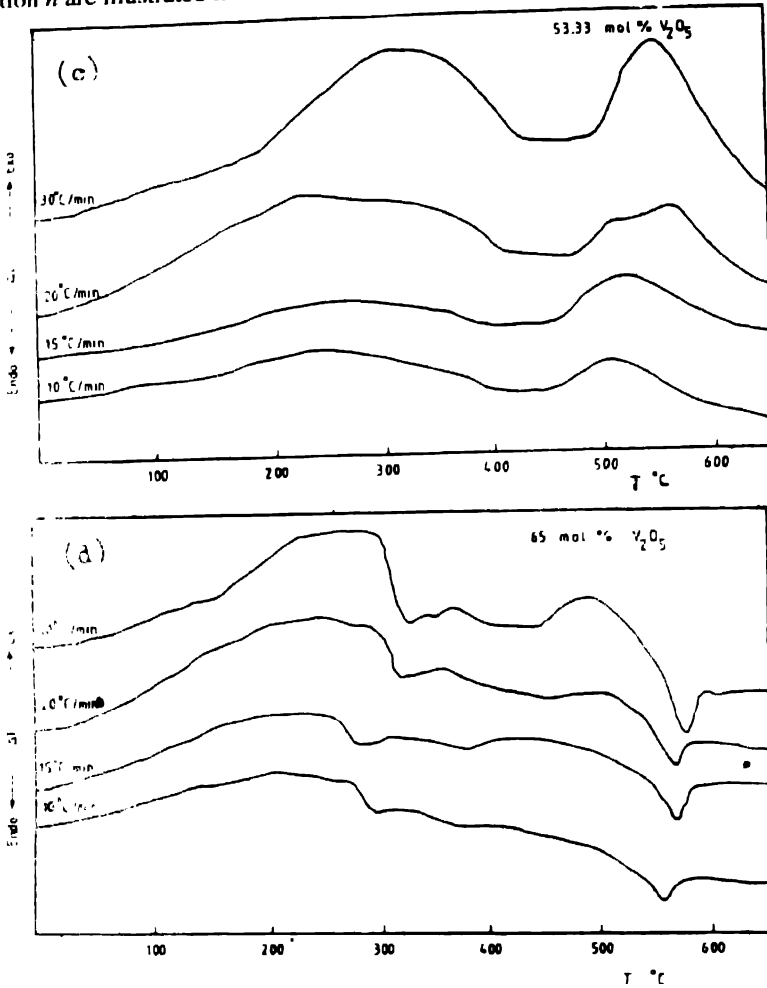


Figure 1. (Continued)

3.2. The effect of composition on DTA peaks observed for V_2O_5/P_2O_5 glasses :

The dependence of the glass-transition temperature (T_g) on the composition of the studied glasses are investigated at fixed heating rate (10, 15, 20 and 30 $^{\circ}C/min$). Figure 3(a) shows the variation of the glass-transition temperature with the V_2O_5 content for the operating different heating rates. The behaviour of the plots in Figure 3(a) revealed three composition regions. The first region shows a rapid decrease in T_g as the V_2O_5 content increases. While in the second region, T_g is slowly decreased as the V_2O_5 content increases. In the third one, T_g is decreased rapidly with increasing V_2O_5 content. It is known that the DTA measurements of the glass-transition temperature (T_g) are useful in suggesting structural changes that take place by compositional change. This is, because T_g is very sensitive to any change of the coordination number of networks-forming atoms (network-former) and

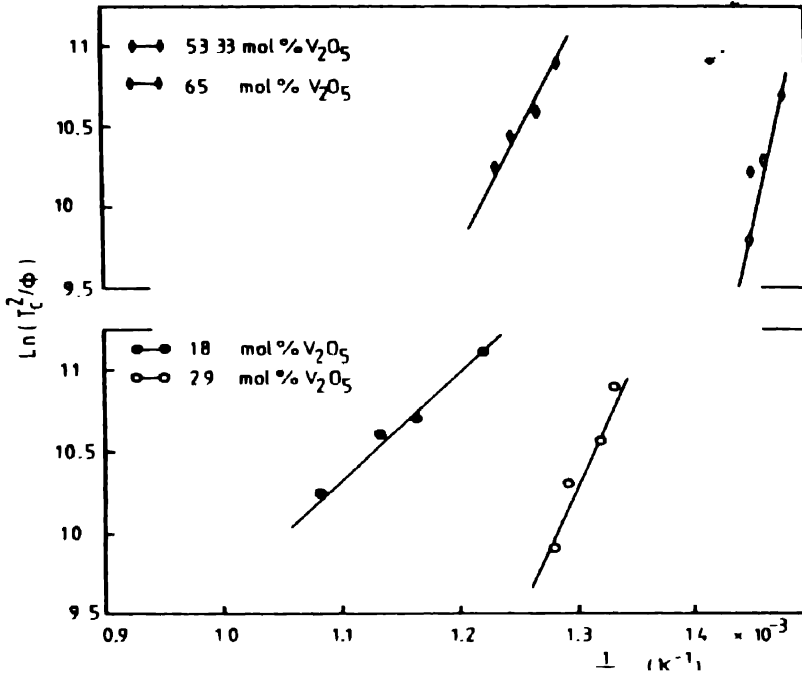


Figure 2(a). The variation of $\ln(T_c^2/\phi)$ with $(1/T_c)$ ($^{\circ}K^{-1}$).

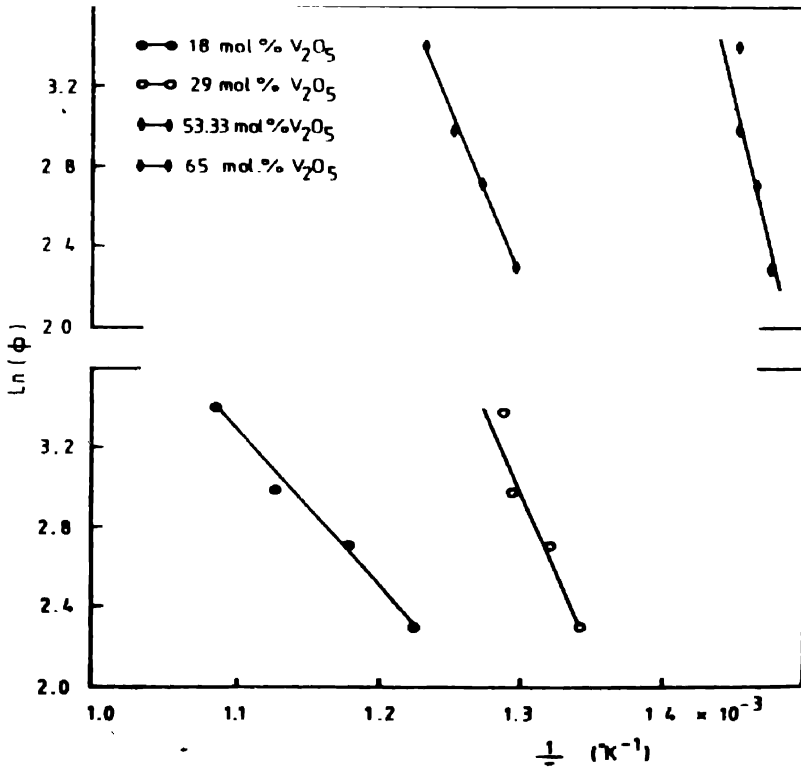
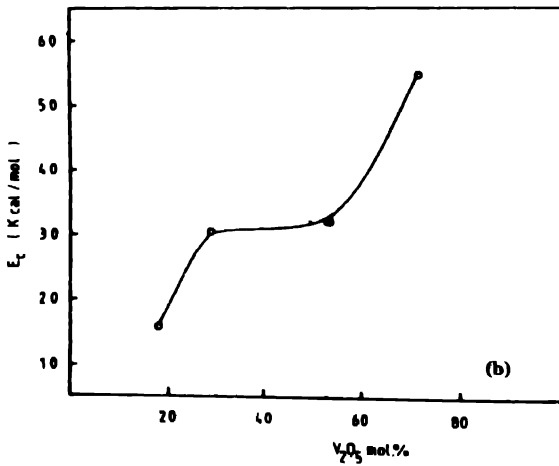
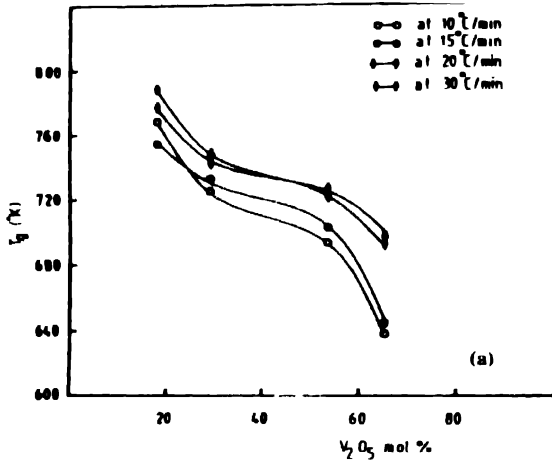


Table I. The values of T_g , T_c , n and E_c at different heating rates for the V_2O_5/P_2O_5 glasses.

V_2O_5 mol%	heating rate f ($^{\circ}C/min$)	T_g $^{\circ}C$	T_c $^{\circ}C$	n	E_c (k cal/mol according to	
					Kissinger	Ozawa
18	10	495	545	1.09	15.68	15.65
	15	482	589	0.85		
	20	505	615	1.22		
	30	515	650	1.19		
29	10	452	475	1.03	30.44	30.43
	15	460	485	1.03		
	20	470	500	1.01		
	30	475	505	1.03		
53.33	10	420	500	1.05	32.25	32.22
	15	430	515	1.04		
	20	452	533	0.93		
	30	450	540	1.32		
65	10	365	405	1.13	45.86	54.89
	15	372	410	1.16		
	20	425	470	1.26		
	30	420	470	1.19		



also to the formation of non-bridging oxygen [9–12], chlorine [8] and fluorine [16] respectively. On the other hand, an introduction of P_2O_5 into V_2O_5 matrix is concluded to three-dimensional network structure composed of the VO_4 [9–12] and also PO_4 tetrahedral [6] respectively. In case of V_2O_5/P_2O_5 glasses, it is speculated that non-bridging oxygen atoms are not formed in the VO_4 tetrahedra [11]. In general, the decrease in the T_g of the present V_2O_5/P_2O_5 glasses, which observed with increasing the V_2O_5 content, are therefore, ascribed to some structural changes which take place in the glass matrix leading to layered structure instead of the three-directional complicated structure. This agrees with previous works [12,6]. The crystallization (ordering) temperature T_c as obtained [6] for some V_2O_5/P_2O_5 glasses, was higher than T_g by about 67°C. This observation has indicated the high stability of the V_2O_5/P_2O_5 glasses. In the present work, the crystallization temperature T_c is also higher than the glass transition temperature T_g by about 85°C, which is consistent with the results reported previously.

The compositional dependence of the activation energy of crystallization for some prepared V_2O_5/P_2O_5 glasses, is shown in Figure 3(b). This Figure indicates three-composition-regions, which are in converse behaviour to that of glass-transition-temperature. The first region shows a rapid increase in the activation energy of crystallization or ordering as the V_2O_5 content increased while in the second one, E_c is slowly increased up to 53 mol% of V_2O_5 . Beyond 53 mol% of V_2O_5 , the activation energy of crystallization E_c shows considerable increase with increasing V_2O_5 content.

Since the compositional dependence of both the glass-transition temperature (T_g) and activation energy of ordering (E_c) has revealed the three-compositional-regions, this is another more evidence which supports all our previous and similar data of density, molar volume, infrared [17] and ultrasonic attenuation of the V_2O_5/P_2O_5 glasses [22].

3.3 Effect of annealing :

In order to investigate the effect of annealing time on the exothermic and endothermic peaks which are observed in all DTA thermograms of the present work; some more DTA and X-ray diffraction measurements were made on the sample which contain 9.33 mol% of V_2O_5 . These measurements were carried out several times after annealing the tested specimen at 350°C for 1, 2, 3, 4, 8, 12, 48 and 96 hours, respectively.

Figure 4(a) shows the X-ray diffraction pattern obtained from the conducted runs of the above investigations. Also, Figure 4(b) shows the results representing the corresponding DTA thermograms. However, X-ray plots [Figure 4(a)] indicate the amorphous nature of the tested V_2O_5/P_2O_5 specimen, since no diffracted peaks have been observed for all measurements after the heat treatment at the different annealing times. Also, the DTA thermograms [Figure 4(b)] reveal two exothermic peaks and an endothermic one between them. The first exothermic peak is characterized by its broadening as occurred in the range of temperature from about 27 to 450°C. This peak is attributed to some sort of relaxation [18] which influences the atomic rearrangements leading to a short range order but no

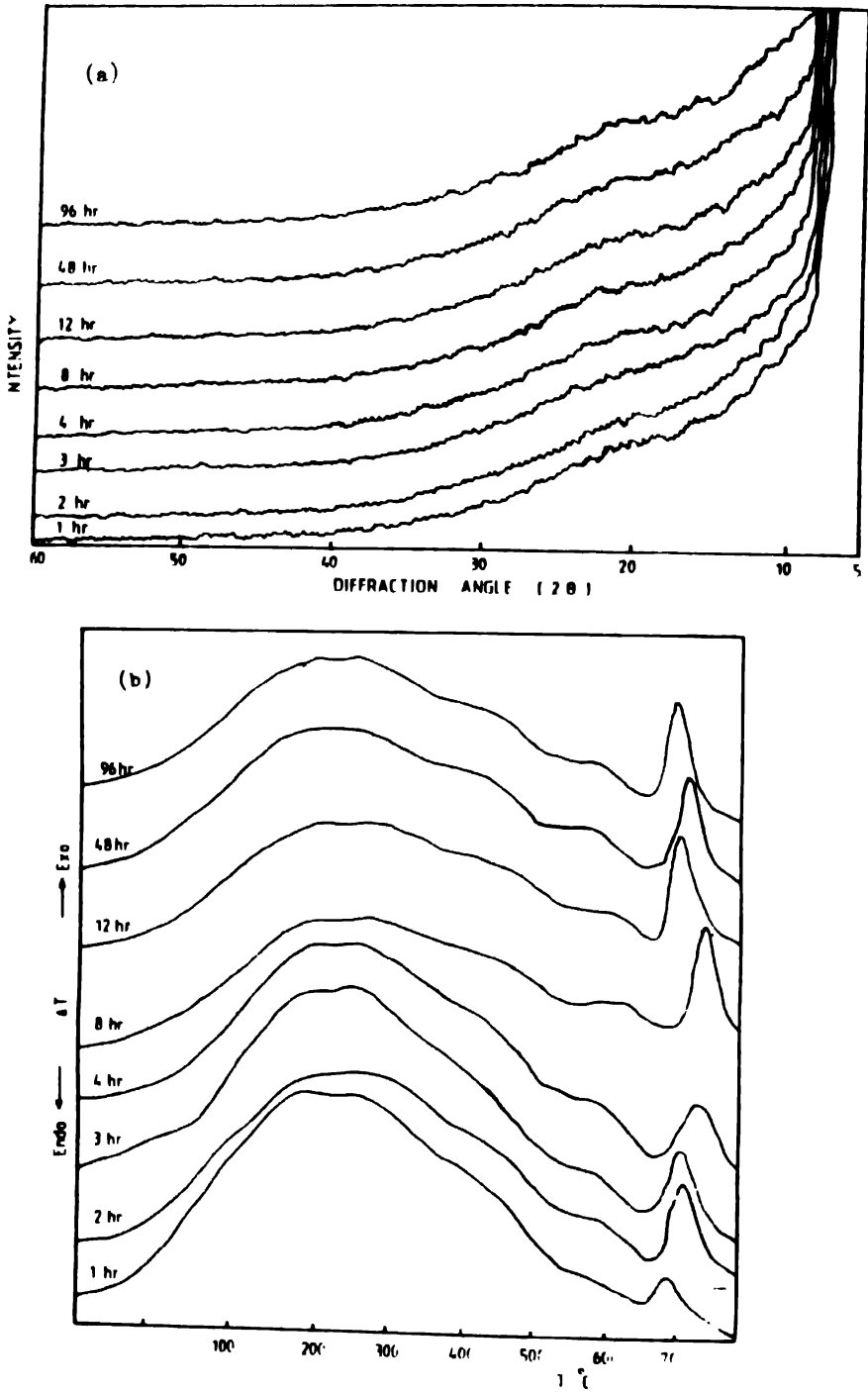


Figure 4. Effect of annealing time on X-ray diffraction and DTA thermograms of V_2O_5/P_2O_5 glass with 9.33 mol% V_2O_5 . (a) and (b) respectively.

crystallization. It is observed that this relaxation peak observed here is affected by the annealing time; its area has changed with annealing time at 350°C as shown in Figure 5(a). Inspection of this Figure shows that as the specimen is annealed, the area of the relaxation peak rapidly decreases up to 10 hours time of annealing. Then, it becomes nearly constant.

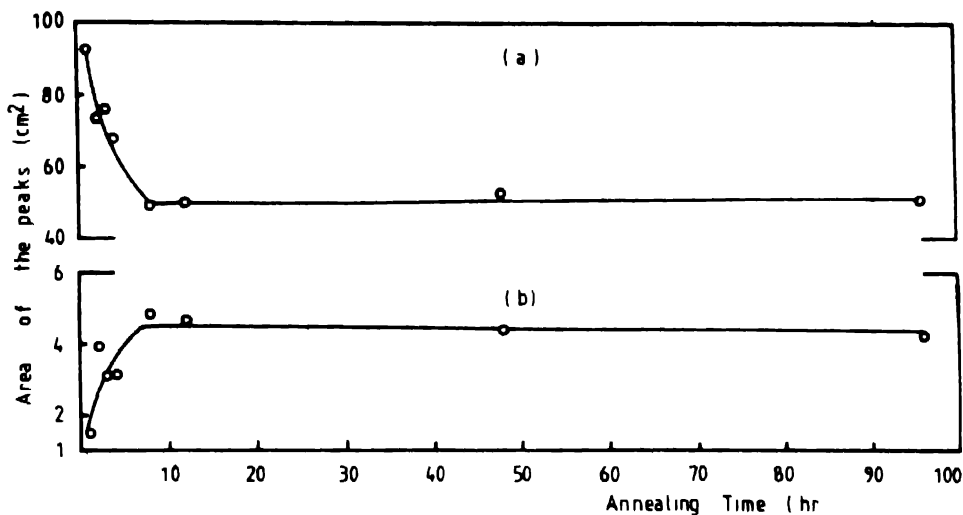


Figure 5. Effect of annealing time on the area of both the relaxation and ordering peaks (a) and (b), respectively

This however, indicates that the quasi-equilibrium state of the tested specimen resulted due to relaxation during heating, can be reached when the specimen is annealed at 350°C for about 10 hours time. The above exothermic relaxation peak is followed by the endothermic one of the glass-transition as shown in Figure 4(b). It is assumed that at a glass-transition, the amorphous state with short range order changes into more random distribution of atoms, and after that the crystallization (long range order) is facilitated. An obvious result for the atomic and the ionic rearrangements which could take place during heating is the observation of the second exothermic peak of crystallization (*i.e.*, long range ordering) after the glass-transition region. The magnitude of this peak is also showed to be dependent on the annealing time, where its area is varied, in a converse sense to that of the relaxation peak [Figure 5(b)], *i.e.*, the area of this peak is increased considerably with annealing time up to 10 hours, then it reached a constant value when the size of the ordered regions in the tested amorphous matrix has attained maximum value after annealing it for 10 hours at 350°C .

4. Conclusion

In the present work, DTA thermograms were carried out in the temperature range $27\text{--}650^\circ\text{C}$, at different heating rates for different composition of V_2O_5/P_2O_5 glasses. These measurements revealed the different phase transitions (*e.g.* glass, crystallization and melting) as well as a relaxation process which occurred during the change in the state of the specimen as the temperature is increased.

Also the effects of heating rate as well as the annealing time on the observed peaks (relaxation and ordering) were investigated. However, the results of the former effects enabled us to determine values for activation energies for both glass and crystallization transitions E_g and E_c respectively.

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