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Structural studies of some V_2O_5–P_2O_5–B_2O_3–Fe_2O_3 glass systems

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X-ray diffraction and infrared measurements were performed on vanadium borophosphate glass containing different amounts of iron ranging from 0–7.5 mol% and heat treated at 300 °C for various times. The structure and phase separation could be determined for each glass composition. V_2O_5 was the main precipitated phase in all heat-treated samples, and its amount was dependent on the heat-treatment time and Fe_2O_3 content. Also FeP was detected in samples heat treated for 24 h. The infrared measurements showed the presence of both V^{4+} and V^{5+}. The symmetry of $V_2O_7^{4-}$ and VO_4^{3-} groups was found to increase with increasing Fe_2O_3 content. It was also found that some PO_4 changed to BO_3, forming a non-bridging oxygen.

1. Introduction

The investigation of the crystallization of glasses is of importance both scientifically and technologically. Glass formation itself implies the avoidance of crystallization during the cooling of a melt. Therefore, study of their physical properties and structure is of great interest.

More complex amorphous semiconductors based on vanadium phosphate have been investigated, and it was found that the stability of such glasses increased as P_2O_5 content increased [1]. Phase separation and/or crystallization in the vanadate glass system has been reported [2, 3]. Limb and Davis [4] showed that V_2O_5 was the main separated phase of vanadium phosphate glasses and it depended on the composition of the glass. Calvo and co-workers [5, 6] determined the crystal structure of two VPO_5 phases. The predominant valence states of vanadium in vanadium phosphate glasses are V^{4+} and V^{5+} and the amount of V^{4+} decreases as the V_2O_5 content increases [7]. It has also been suggested that the loss of oxygen increases with increasing P_2O_5 concentration [8].

The objective of the present investigation was to investigate the microstructure and crystallization process of vanadate glass containing 15 mol% P_2O_5–7 mol% B_2O_3 and different concentrations of Fe_2O_3, using infrared and X-ray diffraction techniques.

2. Experimental procedure

All materials used were of chemically pure grade and in powder form according to the molar formula 68 mol% V_2O_5–15 mol% P_2O_5–17 mol% B_2O_3, and x mol% Fe_2O_3, where $x = 0, 0.5, 1, 2.5, 5$ and 7.5. Vanadium oxide was added as-received, phosphorus pentoxide was introduced as ammonium diahydrogen phosphate $NH_4(H_2PO_4)$, the boric oxide was added in the form of boric acid (H_3BO_3) and the iron oxide was added in the form of Fe_2O_3. The homogeneous mixture was melted for 2 h at 800 °C in an electrically heated furnace and then quenched in air. The glass samples obtained were annealed at 200 °C for 1 h, heat treated at 300 °C for 0.5, 1, 6, 12 and 24 h, and then crushed into powder form for X-ray and infrared investigations. Structural variations were examined by X-rays using a CuK_α radiation source and recorded with a Siemens X-ray diffractometer D-500. The crystalline phases shown by X-ray diffraction (XRD) were identified by comparison with ASTM Cards. The infrared spectra were recorded using a Beckman spectrophotometer IR 4220 in the region between 200 and 4000 cm^{-1}.

3. Results and discussion

In a previous work [9], the effect of heat treatment at 350 °C for various times was studied. V_2O_5 was found to be the main phase separated, and BPO_4 and VO_2 were also detected in some samples. The infrared study showed the presence of both VO_4 and VO_5 groups and both P^{5+} and V^{5+}. The symmetry of $V_2O_7^{4-}$ and VO_4^{3-} groups was found to decrease with Fe_2O_3 content and heat treatment; it was also found that some BO_4 groups changed to BO_3, forming non-bridging oxygens.

In the present work, the effect of heat treatment at 300 °C on the structure was studied.

Figs 1–3 show the X-ray diffraction patterns of the samples free from iron, containing 2.5 and 7.5 mol% Fe_2O_3. XRD showed that the untreated samples were completely in the glassy state, while for heat-treated samples V_2O_5 was detected as the main separated

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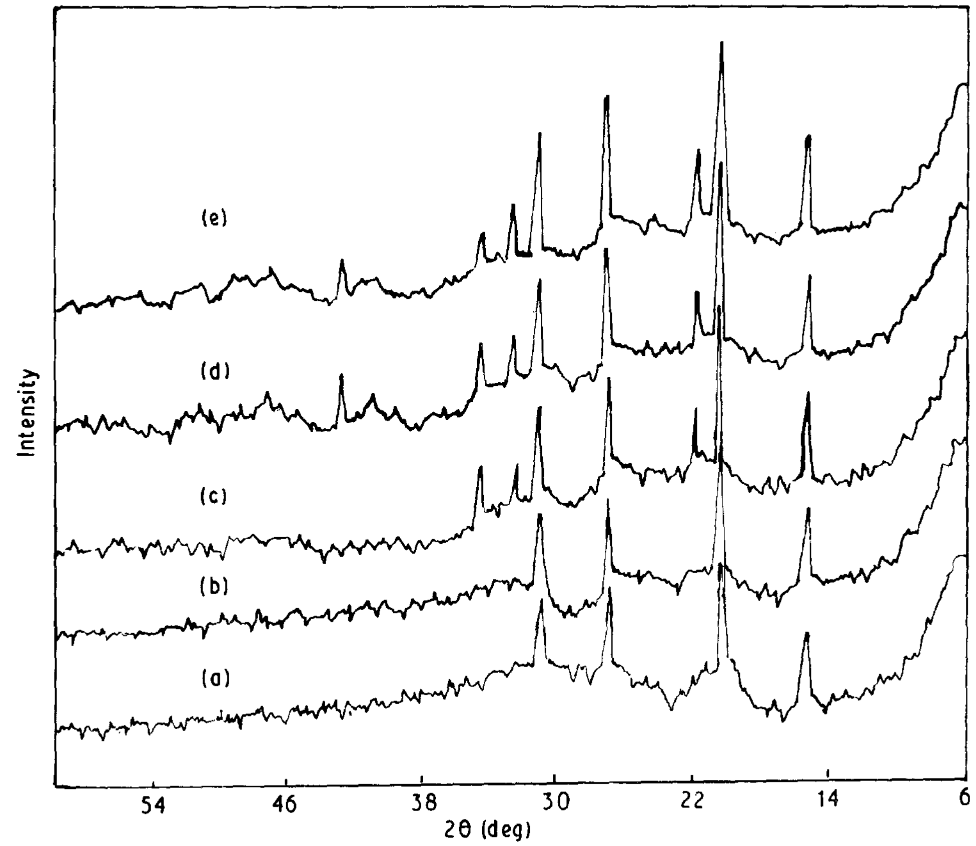

Figure 1 X-ray diffraction patterns of a glass having the composition 68 mol % V_2O_5–15 mol % P_2O_5–17 mol % B_2O_3 and heat treated at 300 °C for (a) 0.5 h, (b) 1 h, (c) 6 h, (d) 12 h, and (e) 24 h.

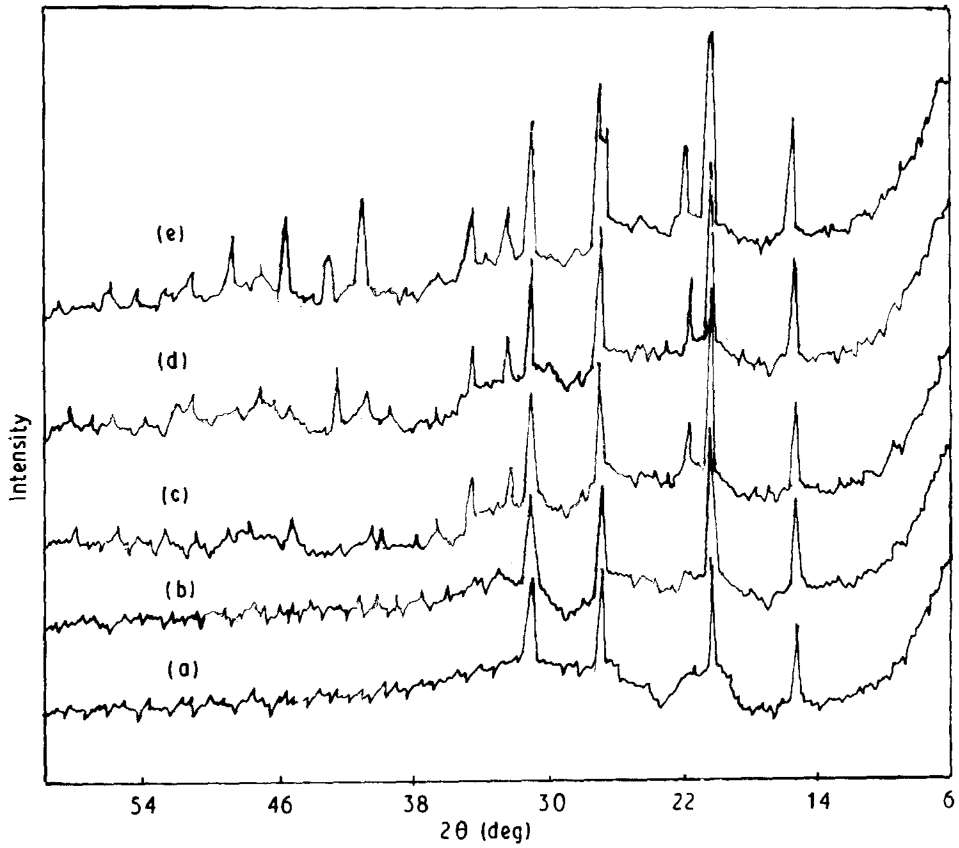

Figure 2 X-ray diffraction patterns of a glass having the composition 68 mol % V_2O_5–15 mol % P_2O_5–17 mol % B_2O_3 and 2.5 mol % Fe_2O_3, heat treated at 300 °C for (a) 0.5 h, (b) 1 h, (c) 6 h, (d) 12 h, and (e) 24 h.

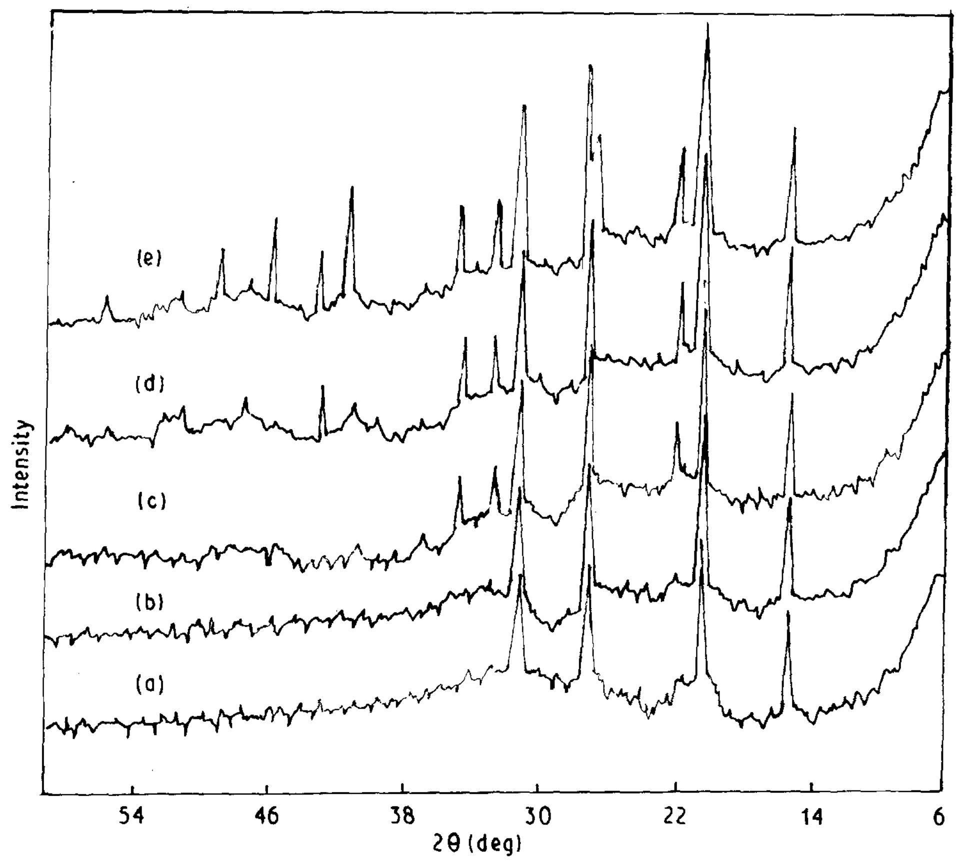

Figure 3 X-ray diffraction patterns of a glass having the composition 68 mol % V_2O_5–15 mol % P_2O_5–17 mol % B_2O_3 and 7.5 mol % Fe_2O_3, heat treated at 300 °C for (a) 0.5 h, (b) 1 h, (c) 6 h, (d) 12 h, and (e) 24 h.

phase, and FeP was detected in samples which contained iron oxide and were heat treated for 24 h. It was also observed that the rate of crystallization of V_2O_5 increased as the heat-treatment time or the Fe_2O_3 content increased. This may be due to the fact that V_2O_5 and Fe_2O_3 may be considered as nucleating agents [10], and the addition of such oxides to a glass system is expected to enhance the rate of uniform nucleation [11]. V_2O_5 also has a higher ionic potential [12]; the addition of Fe_2O_3 increases the ionic potential of the system, and this in turn increases the degree of crystallization [13].

From the above results and previous work, it can be observed that V_2O_5 was the main separated phase in all heat-treated samples (at 350 or 300 °C). In samples heat treated for various times at 350 °C, phases such as BPO_4 were also detected in the sample containing 0.5, 1 and 2.5 mol % Fe_2O_3. In addition, VO_2 and FeP were detected in samples containing 5 mol % (90 min) Fe_2O_3 and also in samples containing 7.5 mol % (60 min) Fe_2O_3. However in the sample heat treated at 300 °C for 24 h, FeP was observed. It is clear that the energy difference needed for separation of the FeP phase had been achieved.

Figs 4 and 5 show the infrared spectra of the samples containing 2.5 and 7.5 mol % Fe_2O_3, heat treated at 300 °C for different times. The infrared spectrum of the sample containing 0.5 mol % Fe_2O_3, heat treated for 0.5 h, the band at 1320 cm^{-1} is due to BO_4 vibration [9]. The band at 1000 cm^{-1} is due to the terminal V–O stretching modes [14, 15], and indicates the formation of isolated bonds and the presence of the symmetric $V_2O_7^{4-}$ and VO_4^{3-} groups [16, 17]. The band at 860 cm^{-1} is due to V–O–V stretching vibration [14, 18], whilst that at 600 cm^{-1} is assigned to bending modes of the PO_4 group [19]. The band at 550 cm^{-1} is assigned to the Fe_2O_4 group [20], and that at 470 cm^{-1} to asymmetric bending modes of the PO_4 unit [21]. The bands at 430 and 415 cm^{-1} are due to coupled V–O and P–O bending modes for both VO_4 and PO_4 groups [14], and the shoulder at 1070 cm^{-1} is due to P–O stretching modes [22]. When this sample is heat treated for 1, 6, 12 and 24 h, the intensity of these bands increases, new bands at 360, 320 cm^{-1}; 675, 520, 360 cm^{-1}; 675 cm^{-1} and 700, 675, 520 cm^{-1} were observed when the samples were heat treated for 1, 6, 12 and 24 h, respectively. The band at 360 cm^{-1} is due to P–O bending modes [5], whilst that at 675 cm^{-1} is due to the doubly degenerate symmetrical deformation of the B–O vibration of boron in three-fold coordination [23]. The band at 520 cm^{-1} is due to symmetric bending modes of PO_4 groups [19], and that at 700 cm^{-1} to the normal vibration frequency of the octahedral V–O bond [24]. At longer heat-treatment times (24 h), the shoulder at 1070 cm^{-1} appeared as a clear band in the same position, indicating that the number of P–O bonds increased as the heat-treatment time increased due to the attraction of bending electrons to the P^{5+} core.

For the heat-treated sample containing 1 mol % Fe_2O_3, it was observed that the same bands appeared in the infrared spectrum of a sample containing 0.5 mol % Fe_2O_3, in addition to the two bands at 680 and 525 cm^{-1}. The band at 680 cm^{-1} is due to P–O asymmetric vibration [25], and that at 525 cm^{-1} is

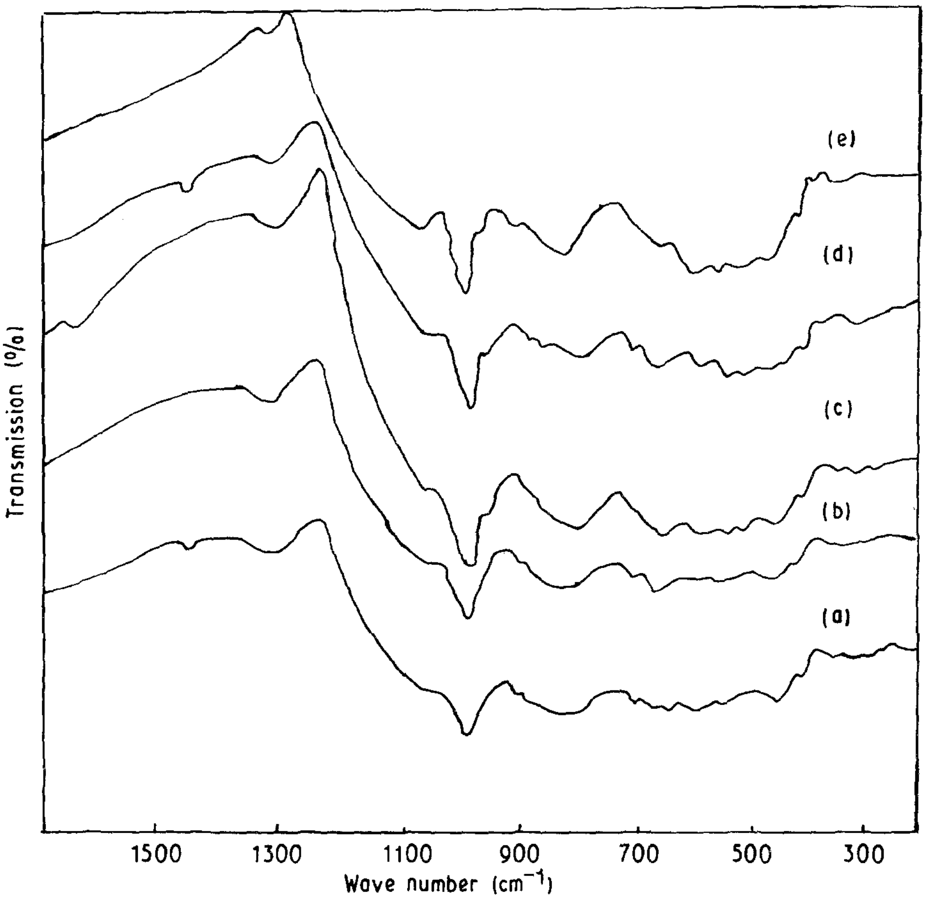

Figure 4 Infrared absorption spectra of a glass having the composition 68 mol % V_2O_5–15 mol % P_2O_5–17 mol % B_2O_3 and 2.5 mol % Fe_2O_3, heat treated at 300 °C for (a) 0.5 h, (b) 1 h, (c) 6 h, (d) 12 h, and (e) 24 h.

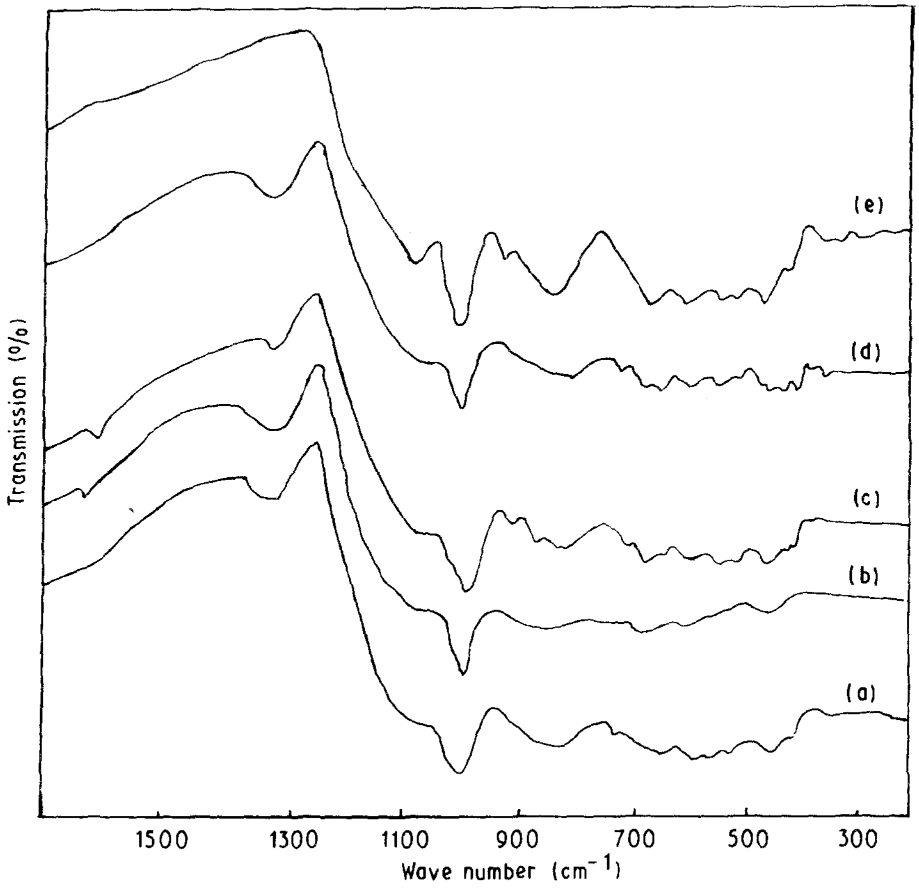

Figure 5 Infrared absorption spectra of a glass having the composition 68 mol % V_2O_5–15 mol % P_2O_5–17 mol % B_2O_3 and 7.5 mol % Fe_2O_3, heat treated at 300 °C for (a) 0.5 h, (b) 1 h, (c) 6 h, (d) 12 h, and (e) 24 h.

due to symmetric bending modes of PO_4 groups [19]. When the sample was heat treated for 1 h, new bands were detected. The band at 645 cm^{-1} is due to symmetric bending modes of PO_4 [9], the band at 440 cm^{-1} is assigned to coupled V–O and P–O bending modes [9], and the band at 675 cm^{-1} is due to boron in three-fold coordination [23]. When the sample was heat treated for 6 and 12 h, new bands at 660 and 330 cm^{-1} were observed, in addition to the band at 725 cm^{-1} which was also observed when the sample was heat treated for 12 h and which is due to B–O–B bending modes [26]. The shoulder at 1070 cm^{-1} changed to a clear band at 1080 cm^{-1} when the sample was heat treated for 24 h, and a new band at 385 cm^{-1}, which is due to the VO_4 group [27], was observed, in addition to a shoulder at 925 cm^{-1} due to P–O and V–O stretching modes of the resulting linked PO_4 and VO_5 unit [9].

The infrared spectra of the heat-treated samples containing 2.5 mol % Fe_2O_3, show some new bands: one at 1460 cm^{-1}, which is due to boron tetrahedra [9], and one at 840 cm^{-1}, which is due to B–O–B nonbridging vibration [28]. The band at 985 cm^{-1}, is due to symmetric and antisymmetric stretching vibration of isolated nonbridging oxygens of the VO_2 group in the VO_4 polyhedra [29]. When the sample was heat treated for 1 h, a new band at 675 cm^{-1} was observed. The band at 850 cm^{-1} is assigned to the V–O–V stretching modes [29], whilst that at 555 cm^{-1} is due to the Fe_2O_4 group [20], and that at 450 cm^{-1} is due to V–O and P–O bending modes [14]. A new band at 1620 cm^{-1} due to P_4O_{10} group vibration [29], one at 1415 cm^{-1} which is due to vibration of boroxol rings [28], and a shoulder at 910 cm^{-1} which is due to nonbridging oxygens of the VO_2 group vibration [29], were observed when the sample was heat treated for 6 h. The infrared spectrum of the sample heat treated for 12 h shows new bands at 1445, 675, 410, 385 and 360 cm^{-1}, and some bands shifted to higher frequencies. The band at 1445 cm^{-1} is due to >B–O–B– vibration [30]. No essential changes could be observed in the infrared spectra when the sample was heat treated for 24 h, the only change being that the shoulder at 1070 cm^{-1} changed to a clear band at the same position.

The infrared spectra of heat-treated samples containing 5 and 7.5 mol % Fe_2O_3 show an increase in the intensity of the different bands with increasing heat-treatment time, the presence of BO_3 groups in addition to BO_4 groups, as indicated by the presence of bands at 1310 and 675 cm^{-1}, the presence of Fe_2O_4 groups due to the presence of the band at 550 cm^{-1} and the change of the shoulder at 1070 cm^{-1} to a clear band when the sample was heat treated for 24 h.

The infrared measurements showed that the introduction of iron oxide to the glass samples causes the formation of non-bridging oxygens and tetrahedral groups (boron exists in three and four coordination). It also showed that the V–O bond has been observed in the glassy state as V^{5+} ions and exists in six-fold coordination as in the crystalline state. The heat treatment weakens the V–O bond and the bending electrons are attracted to the P^{5+} core, the formation of V–O short isolated bonds and increasing the symmetry of $V_2O_7^{4-}$ and VO_4^{3-} groups due to the increase in the type of bond. In a sample heat treated for 350 °C for various times up to 2 h, the symmetry of $V_2O_7^{4-}$ and VO_4^{3-} was found to decrease with heat treatment which may break the V–O short bonds.

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