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An infrared study of the Na_2O–V_2O_5–Fe_2O_3 glass system

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Structural studies of Na_2O–V_2O_5–Fe_2O_3 glasses have been made from their IR spectra which show that vibrational bands characteristic of the vanadium–oxygen bonds in V_2O_5 are maintained in these glasses, but the addition of Na_2O to these glasses results in a shifting of the higher frequency peaks towards lower wave number due to structural changes produced in V_2O_5. It is inferred that Na^+ ions make bonds interstitially with isolated V=O bonds and VO_5 polyhedra are destroyed, resulting in the formation of VO_4 polyhedra through intermediate complexes. The variation of Fe_2O_3, however, produces an insignificant structural change in these glasses. The IR spectra of samples heated to their temperature of crystallization confirm the formation of a series of complexes with several isolated V=O bonds.

1. Introduction

Infrared spectroscopy is one of the important techniques used to study the molecular structure of inorganic glasses. It has been used in the past to draw inferences about the structure of borate, silicate and phosphate glasses [1–4]. This technique can also be employed for structural studies of vanadate systems in crystalline as well as amorphous states, because of characteristic vibrations of these isolated vanadium–oxygen bonds in the 1025 to 900 cm^{-1} range. Several conclusions have already been obtained on this basis about the structure of glasses of V_2O_5–P_2O_5 [4–6], BaO–ZnO–V_2O_5 [7], V_2O_5–TeO_2 [8], V_2O_5–B_2O_3 [9, 10], Na_2O–V_2O_5–TeO_2 [11, 12], K_2O–V_2O_5–$2TeO_2$: $2TeO_2$–V_2O_5 [13], B_2O_3–V_2O_5–P_2O_5 [14] and V_2O_5–P_2O_5–TeO_2 [15].

In the present work, structural studies of Na_2O–V_2O_5–Fe_2O_3 glass systems have been made from IR spectroscopy. These glass samples were also heat-treated at their respective crystallization temperatures (determined by differential scanning calorimetry (DSC)) and were used to study the presence of a series of complexes of crystalline phases formed by interaction of Na^+ ions with isolated V=O bonds. The formation of these crystalline phases has also been confirmed from X-ray diffraction analysis.

2. Experimental techniques

Analytical grade Na_2CO_3, V_2O_5 and Fe_2O_3 were weighed and melted in porcelain crucibles at 800° C for 6 to 8 h. The melt was poured onto a clean copper plate and rapidly pressed by another copper plate for faster quenching. The solid samples were crushed to powder form to obtain X-ray diffraction spectra and the amorphous nature of these samples was confirmed. A few milligrams of glass powder were mixed and ground with a relatively large quantity of KBr to obtain IR spectra. KBr pellets, which are transparent to IR radiation, were formed by pressing the mixture under a pressure of ~ 1 ton/cm^2 in vacuum for a few minutes. The infrared spectra were obtained by using a Perkin-Elmer 580-B IR spectrophotometer. Thermograms of all the samples were obtained on a DuPont differential scanning calorimeter. The glass samples were sintered for 12 h at different temperatures depending upon their temperature of crystallization as determined by DSC. X-ray diffraction spectra were obtained from the sintered glasses on a Philips X-ray spectrometer to ascertain the possible presence of any crystalline phases on a microcropic scale.

3. Results and discussion

Molecular structural investigations were carried out by IR spectroscopy for the following three glass systems with different compositions:

(i) $x Na_2O:(90 - x)V_2O_5:10Fe_2O_3$
(ii) $y Na_2O:(85 - y)V_2O_5:15Fe_2O_3$
(iii) $z Fe_2O_3:(100 - z)(Na_2O:2V_2O_5)$

where x varies from 20 to 40 mol %, y varies from 15 to 35 mol % and z varies from 5 to 22.5 mol %. Mössbauer studies of systems (i) and (ii) have already been reported by the authors [16, 17] which indicated that iron goes to tetrahedral as well as octahedral sites by an amount which depends upon the structural changes produced due to the different concentrations of Na_2O in these series. The changes in the structure of V_2O_5 can, however, be determined by the IR technique.

The IR spectrum of pure crystalline V_2O_5 (Fig. 1a) shows the presence of the following absorption bands: (i) 1025 cm^{-1}, which is characteristic of the isolated V=O bond of VO_5 polyhedra; (ii) 830 and 620 cm^{-1} which are due to symmetric and anti-symmetric vibrational modes of the V–O–V group; and (iii) 480 cm^{-1} which is attributed to the angular deformation mode δO–V [18]. The IR spectrum of amorphous V_2O_5, (Fig. 1b) shows these peaks at the same wave numbers and are broadened due to short-range order, which is also in agreement with similar inferences drawn by

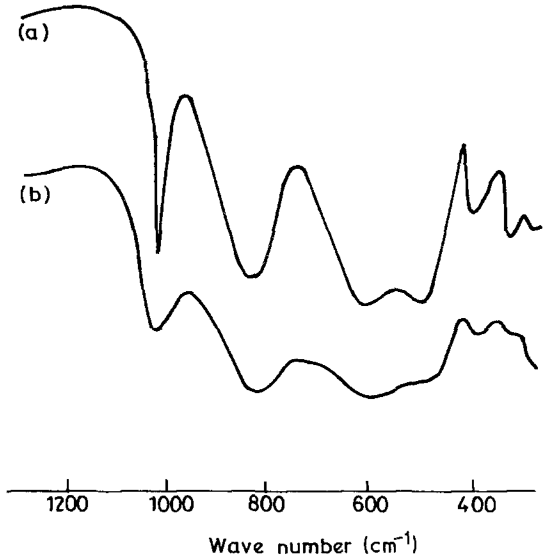

Figure 1 IR spectra of (a) pure crystalline V_2O_5, (b) amorphous V_2O_5.

Dimitriev *et al.* [11]. Sayer and Man Singh [4] have shown that IR features which are characteristic of vanadium–oxygen bonds in pure crystalline V_2O_5 are also maintained in vanadate glasses. A similar trend is also observed in the present work, as shown in Figs 2 to 4. As the concentration of Na_2O, x, is increased successively from 20 to 40 mol % in the glass system $xNa_2O:(90 - x)V_2O_5:10Fe_2O_3$, the IR spectra (Fig. 2) show that the high-frequency absorption band gets shifted from 1000 to 945 cm^{-1}. Also the peak at 830 cm^{-1} shifts to 780 cm^{-1} whereas the peak at 620 cm^{-1} shifts to 630 cm^{-1}. The peak of the angular mode δO–V, however, remains unchanged at 480 cm^{-1}. All these bands are significantly broadened because of short-range order, and such shifting in position of the peaks is attributed to changes produced in the sturcture of V_2O_5 due to the addition of Na_2O.

The IR spectra of the system $yNa_2O:(85 - y)V_2O_5:15Fe_2O_3$ (Fig. 3) show a similar trend of shifting of the high-frequency peak from 1010 to 945 cm^{-1}. In order to find the effect of Fe_2O_3 on these glasses, the series $zFe_2O_3:(100 - z)(Na_2O:2V_2O_5)$ was studied in which the ratio of Na_2O and V_2O_5 was kept constant as 1 : 2 and the amount of Fe_2O_3 was varied from 5 to 22.5 mol %. No change was observed in the IR spectra of these glasses (Fig. 4). The broad peaks of vibrations observed at 970, 780, 630 and 480 cm^{-1} in all the samples of this series confirm that Fe_2O_3 does not have any significant effect on the IR spectra of the $Na_2O–V_2O_5–Fe_2O_3$ glass system.

The shifting of the high-frequency band of the V=O bond towards lower wave number can be attributed to changes in the structure of V_2O_5 produced by the addition of Na_2O [19]. When Na_2O is introduced, Na^+ ions go either to interstitial or substitutional sites in vanadate chains; this would influence the isolated V=O bond and thus affect the vibrations of V=O bonds depending upon the position of the Na^+ ions. If Na^+ ions occupy substitutional sites V–O–V bonds will break up and form V–O–Na bridges which would restrict the influence of Na^+ ions on V=O bonds, thus preserving the position of the vibrational frequency at 1025 cm^{-1} in the IR spectrum.

In the case where Na^+ ions are going interstitially in vanadate chains, these will interact directly with isolated V=O bonds and thus shift the vibrational frequency towards lower wave numbers because the V=O bonds become longer. Since the high-frequency absorption bands observed in the IR spectra shift towards lower wave numbers with increase of Na_2O, this shows that Na^+ ions, which are electrostatically charged particles with spherical symmetry, make bonds only interstitially with isolated V=O bonds. The addition of Na_2O to these glasses results in the formation of a series of complexes with more than one V=O bond, having vibration frequencies close to each other [19]. As these overlapping bands cannot be resolved, a broad maximum is observed which shifts towards lower frequency with increase of Na_2O due to the destruction of vanadate layers. It had been

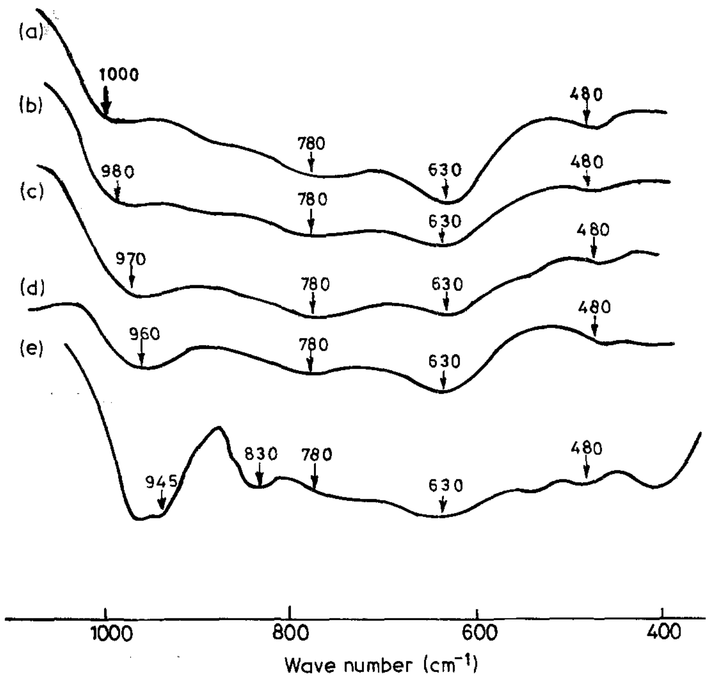

Figure 2 IR spectra of $xNa_2O:(90 - x)V_2O_5:10Fe_2O_3$ glass series. x = (a) 20, (b) 25, (c) 30, (d) 35, (e) 40.

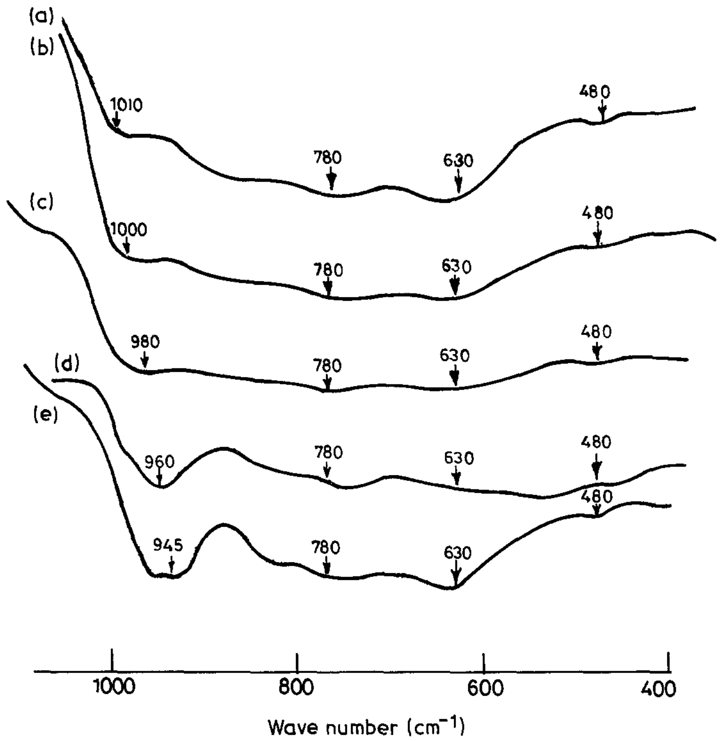

Figure 3 IR spectra of $y\text{Na}_2\text{O}:(85 - y)\text{V}_2\text{O}_5:15\text{Fe}_2\text{O}_3$ glass series, y = (a) 15, (b) 20, (c) 25, (d) 30, (e) 35.

concluded from the Mössbauer study [17] of these samples that VO_5 groups are destroyed and that the main structural polyhedron VO_4 forms chains with longer bonds. The IR spectra of these metavanadate glasses therefore contain only one high-frequency band, which is attributed to stretching vibrations of the VO_2 groups of VO_4 polyhedra.

In order to explain the formation of a series of complexes with several V=O bonds in the glasses, DSC thermograms of these glass samples were taken. It was observed that these glasses possess two to three crystallization temperatures, T_c, along with one endothermic peak at the glass transition temperature, T_g. Samples were heat-treated at temperatures corresponding to their different crystallization temperatures, and their IR spectra were taken in the range 1400 to 300 cm^{-1}. Typical spectra for the heat-treated samples, corresponding to $x = 20$ and $y = 35$ in

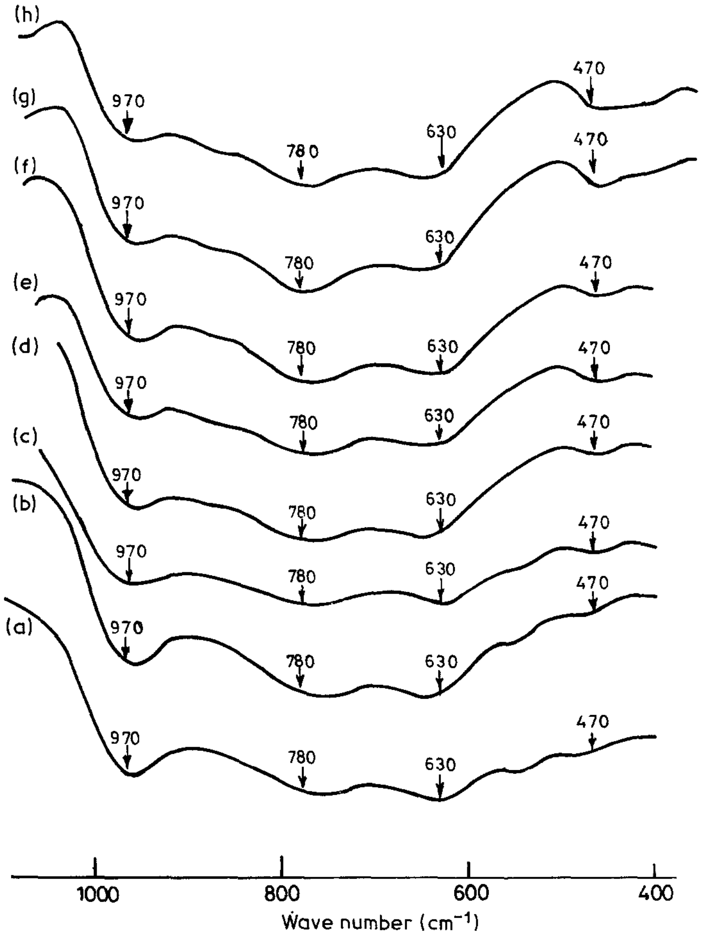

Figure 4 IR spectra of $z\text{Fe}_2\text{O}_3:(100 - z)(\text{Na}_2\text{O}:2\text{V}_2\text{O}_5)$ glass series. z = (a) 5.0, (b) 7.5, (c) 10.0, (d) 12.5, (e)15.0. (f) 17.5, (g) 20.0, (h) 22.5.

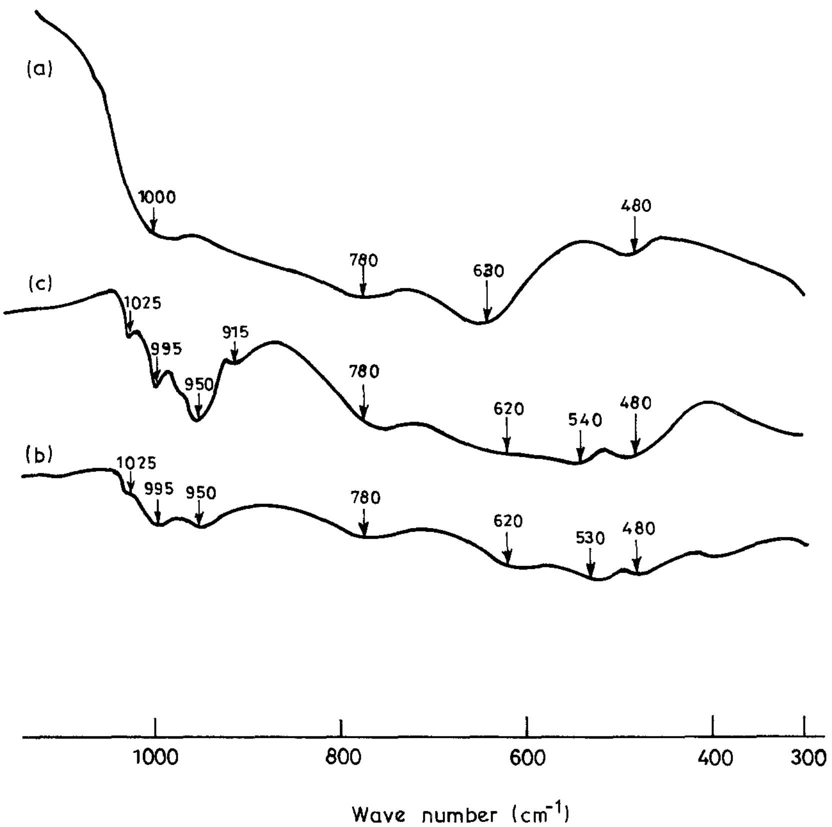

Figure 5 IR spectra of amorphous and heat-treated sample, $x = 20$. (a) Original, (b) T_{c_1}, (c) T_{c_2}.

systems (i) and (ii), respectively, are shown in Figs 5 and 6.

The IR spectrum of the original amorphous $x = 20$ sample (Fig. 5) shows peaks at 1000, 780, 630 and 480 cm^{-1}. The IR spectrum of a sample given heat treatment at the temperature of its first crystallization, T_{c_1}, shows broad vibration peaks at 1025, 995, 950, 780, 620, 530 and 480 cm^{-1}. When heat-treated at the second crystallization temperature, T_{c_2}, the sample shows a new sharp peak at 915 cm^{-1} and the peaks already present in the spectrum become sharper. The decrease in width of such peaks indicates the presence of increased long-range order in these glasses. Therefore, the emergence of new peaks at 1025, 995, 950 and 915 cm^{-1}, which were absent in the amorphous states of this sample, show further interactions of Na^+ ions with the V=O bond, making some new types of complex of sodium vanadium oxide in the glass structure. This was also confirmed from X-ray diffraction of these samples [20]. The peak at 540 cm^{-1} shows the formation of Fe_2O_3 after crystallization.

The sample having $y = 35$ was similarly heat-treated at three different temperatures corresponding to the respective temperatures of crystallization. It is

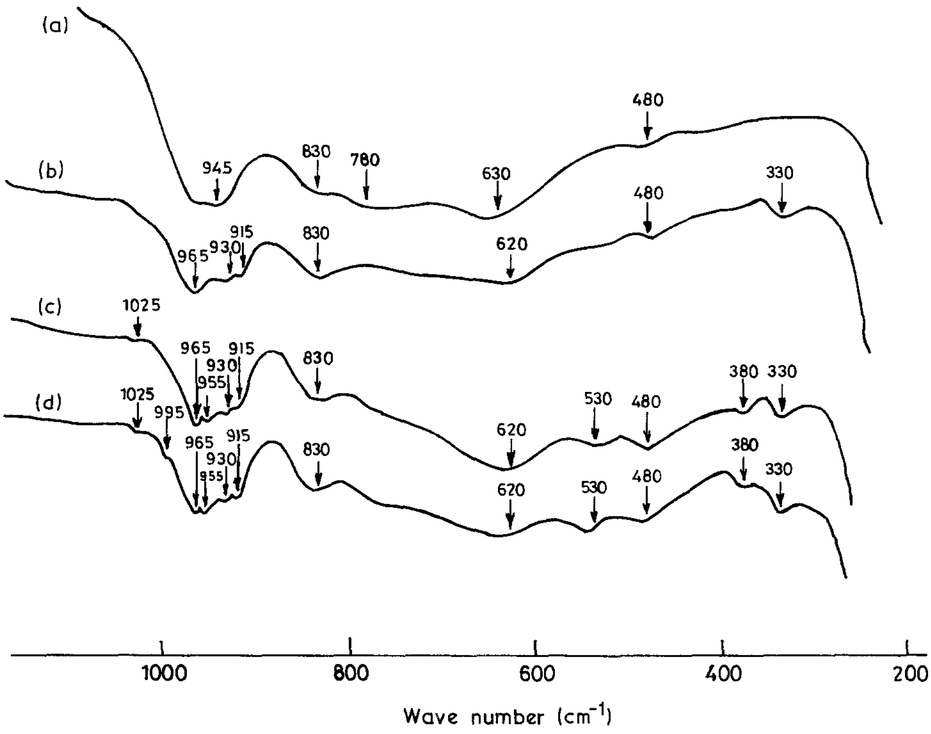

Figure 6 IR spectra of amorphous and heat-treated sample, $y = 35$. (a) Original, (b) T'_{c_1}, (c) T'_{c_2}, (d) T'_{c_3}.

evident from the IR spectra (Fig. 6) that the vibration peaks at 965, 930, 915, 830, 620, 480 and 330 cm^{-1} are present only at T'_{c_1}, and new vibrational peaks are observed at 1025, 955, 530 and 380 cm^{-1} at the second temperature T'_{c_2}; an additional new peak appears at 995 cm^{-1} at temperature T'_{c_3}. These peaks become successively sharp at higher temperatures, indicating an increased crystallinity.

The emergence of new peaks in the range 1025 to 900 cm^{-1}, which have been assigned to the characteristic vibrations of the isolated V=O bond, indicates clearly the formation of several crystalline phases in the region between V_2O_5 and $NaVO_3$ [19, 20]. The successive increase of Na_2O in these glasses makes it possible to form a series of complexes in the glasses. These complexes contain more than one short V=O bond, having close absorption frequencies in the range 1025 to 900 cm^{-1} which are observed in these crystallized samples. When the amount of Na_2O, x, is equal to 20 mol %, the vibrational frequencies are observed at 1025, 995, 950 and 915 cm^{-1}, whereas for the sample having a large amount of Na_2O, y = 35 mol %, the interaction of Na^+ with the V=O bond is more pronounced and results in the formation of additional new complexes. This results in the appearance of IR bands at 965 and 930 cm^{-1}.

It can be concluded from the present IR studies of this system that Na^+ ions go interstitially and interact directly with the isolated V=O bonds. The shifting of the high-frequency band towards lower wave number with the addition of Na_2O indicates that VO_4 polyhedra are being formed with the destruction of VO_5 polyhedra, resulting in the formation of a series of complexes with several short isolated V=O bonds.

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