DSC and spectroscopic studies of the structure of V_2O_5–CdO–P_2O_5 glasses

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xV_2O_5–(50-x)CdO–$50P_2O_5$ ($0 \le x \le 50$ mol%) glasses were prepared and investigated using DSC, IR spectroscopy and Raman spectroscopy. For low concentrations of V_2O_5 ($x \le 20$ mol %), the formation of P–O–V bonds increases the cross-link strength of the glass network and leads to increased T_g. For $x > 20$ mol%, the infrared and Raman spectra show that the vanadium−oxygen structural units formed in the glasses are VO_5 and VO_4 groups forming chains with V−O−V bridges. The formation of the weaker V−O−V bonds compared with the stronger P–O–P bonds leads to decreased T_g.

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1. Introduction

P_2O_5 is considered as one of the glass forming oxides whereas V_2O_5 is a conditional glass former [1]. Growing attention has been given in the last decade to phosphate glasses containing V_2O_5 [2-6]. There is a considerable practical interest in these glasses due to their optical properties [7] and their electrical properties [8-10]. The structure of these glasses has been the object of different studies. The determination of structure of amorphous solids is a difficult task and usually requires a combination of experimental techniques. Thus, for vanadophosphate glasses, EXAFS [11], XANES [12] and Raman spectroscopy [2, 4] have shown the presence of VO_4 and/or VO_5 and PO_4 units which are connected to each other via oxygen bridges to form a three dimensional network. The structural role of V_2O_5 in many oxide glasses is known to play a dual structural role both as a network modifier and as a network former [13]. V_2O_5 when mixed with glass former like B_2O_3, P_2O_5, TeO_2 form stable glasses in comparatively wide range of compositions [14]. The studies on glasses containing CdO and V_2O_5 together are few [15-17]. These types of glasses have gained special interest because of their mixed electronic (via electron hopping between V^{4+} and V^{5+} ions) and ionic (via Cd^{2+} ions) conductivity [15]. In the present paper we report the results of a study of the relationship between the structure and glass transition temperature of V_2O_5–CdO–P_2O_5 glass system with the aid of infrared spectroscopy and Raman spectroscopy.

2. Experimental procedure

The xV_2O_5–(50-x)CdO–$50P_2O_5$ samples were prepared from stoichiometric powders resulting from the mixing of $CdCO_3$, V_2O_5 and $(NH_4)_2HPO_4$ ($0 \le x \le 50$ mol% V_2O_5). The oxidation and reduction reactions in a glass melt are known to depend on the size of the melt, the sample geometry, the concentration of total redox ions, thermal history and quenching rate [18, 19]. To keep these parameters constant, all glass samples were prepared under the same conditions as follow.

After mixing a batch of about 12 g with prescribed compositions, the mixed mass of each glass composition was melted in an alumina crucible for 2 h at 500 °C in an electric furnace in order to evaporate ammonia, carbonate and water in the batch, and minimize the tendency of subsequent phosphate loss. Next, the temperature was raised gradually to 1000 °C and held constant at this value for 30 min to homogenize the melt. The molten glasses were then quenched to room temperature under air atmosphere. The glasses were then stored under vacuum in a desiccator over silica gel until use.

3. Characterization procedure

The X-ray diffraction (XRD) patterns of the samples were recorded using a Philips (X'PERT- PRO) diffractometer. The glass transition temperatures (T_g) were determined using differential scanning calorimeter (DSC SETARAM 121) at heating rate of (10 °C.min^{-1}) under argon atmosphere, these temperatures are reproducible to ± 5 °C.

The IR spectra of the samples were recorded at room temperature in the range 400–1400 cm^{-1} by the standard KBr pellet disc method using a Fourier transform infrared (FT-IR) spectrometer (BRUCKER Tensor 27). The glass samples were ground in a clean mortar as fine powder. Small quantities of glass powder were mixed and ground with KBr in the ratio 1/25. KBr pellets of thickness 1 mm were formed by pressing the mixture at 15 tons for a few minutes. All spectra were run at 4 cm^{-1} resolution.

The Raman spectra were measured in the range 200-1400 cm^{-1} with a Horiba Jobin Yvon Micro-Raman spectrometer (LABRAM Dilor) coupled to an internal laser He-Ne (18 mW) using the 632.8 nm line and to an external Spectra-Physics laser Ar^+ (200 mW) using the 514.5 nm line.

4. Results

The XRD patterns of all glass samples are shown in Fig. 1. The figure exhibits a broad diffuse scattering at low angles instead of crystalline peaks, confirming a long-range structural disorder characteristic of amorphous network.

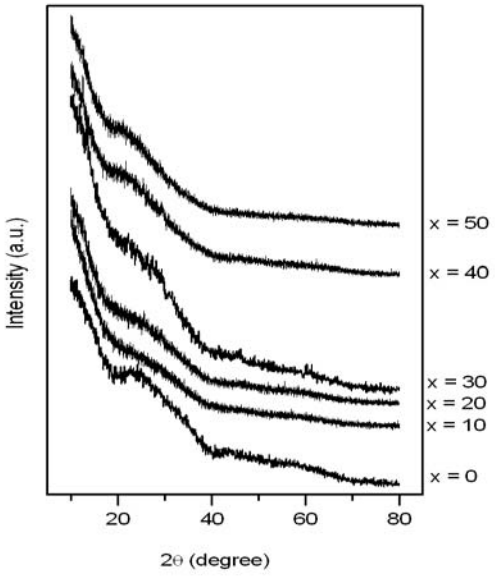

Fig. 1. X-ray diffractograms of xV_2O_5─(50-x)CdO─$50P_2O_5$ glasses.

Fig. 2 shows the composition dependence of the glass transition temperature T_g with V_2O_5 content in the xV_2O_5–(50-x)CdO–$50P_2O_5$ glass system. Two different regimes can be observed in the glass transition temperature variations. For low vanadium oxide concentrations ($0 \le x \le 20$), T_g increases from 473 to 495 °C. Further increase of V_2O_5 concentration above 20 mol% shows a decrease in the glass transition temperature from 495 °C in $20V_2O_5$–$30CdO$–$50P_2O_5$ glass to 440 °C in $50V_2O_5$–$50P_2O_5$ glass.

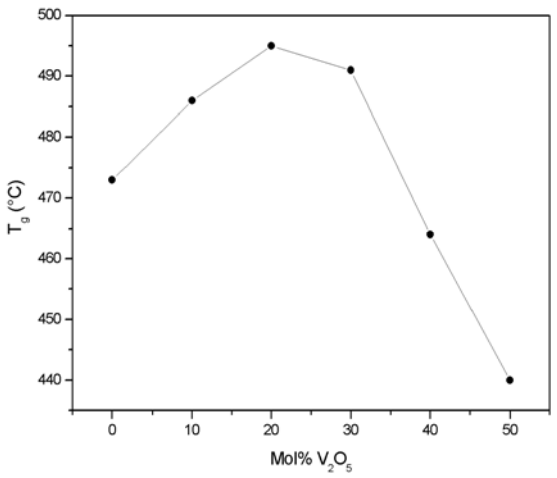

Fig. 2. Composition dependence of glass transition temperature, T_g, for xV_2O_5─(50-x)CdO─$50P_2O_5$ glasses.

The FTIR spectra of xV_2O_5─(50-x)CdO─$50P_2O_5$ glasses ($0 \le x \le 50$ mol%), in the frequency range between 400 and 1400 cm^{-1} are shown in Fig. 3. The spectrum of the $50CdO$─$50P_2O_5$ glass shows a FTIR pattern typical of metaphosphate chain structure [20, 21]. Its characteristic features are the PO_2 asymmetric stretching vibration band at 1273 cm^{-1}, the PO_2 symmetric stretching vibration band at 1150 cm^{-1}, the ν_{as} of PO_3 groups (chain end) at 1082 cm^{-1} , the ν_s of PO_3 groups at 1030 cm^{-1}, the ν_{as} of POP groups at 893 cm^{-1}, the ν_s of POP groups at 775 and 720 cm^{-1} and the bending vibration (δ) of P–O bonds at 520 and 473 cm^{-1} [22-24].

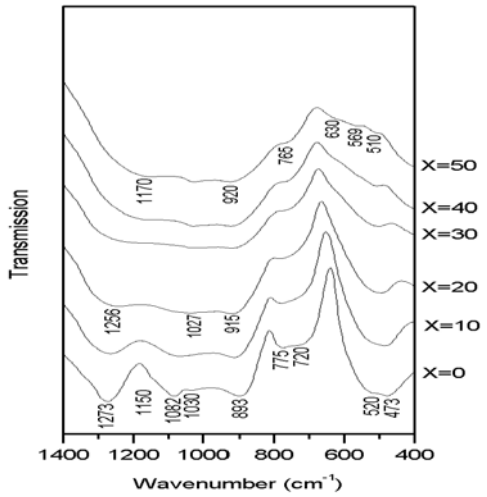

Fig. 3. Infrared spectra of xV_2O_5─(50-x)CdO─$50P_2O_5$ glasses.

The main feature of the infrared spectra of the glasses with $0 \le x \le 20$ mol% V_2O_5 (Fig. 3) is the decrease of the intensity of PO_2 asymmetric stretching vibration band and

of ν_{as} and of ν_s P−O−P bridges when x increases from 0 to 20 mol% V_2O_5. These changes in the spectra of the glasses with V_2O_5 addition are due to the decrease of average phosphate chain length [22]. Absorption band of PO_2 asymmetric stretching mode shifts from 1273 cm^{-1} in $50CdO{-}50P_2O_5$ glass to 1256 cm^{-1} in $20V_2O_5{-}30CdO{-}50P_2O_5$ glass. The band arising from the P−O−P asymmetric stretching mode shifts to higher frequency from 893 cm^{-1} (for $50CdO{-}50P_2O_5$) to 915 cm^{-1} (for $20V_2O_5{-}30CdO{-}50P_2O_5$).

For high vanadium concentrations (x ≥ 20 mol%), the PO_2 asymmetric stretching vibration band at 1256 cm^{-1} for x = 20 mol% V_2O_5 gradually disappears by integration into 1170 cm^{-1} band in the $50V_2O_5{-}50P_2O_5$ glass. This result indicates that no more phosphate chains remain in the glasses with x ≥ 20 mol% V_2O_5 [25]. It is interesting to note that the glasses with x ≥ 20 mol% V_2O_5 exhibit only a single band at 765 cm^{-1} which is assigned to the P−O−P linkage in pyrophosphate group ($P_2O_7^{4-}$) [26]. The in-chain P−O−P asymmetric and symmetric decrease in intensity indicating that the number of in-chain P−O−P bonds is diminishing with the increase of V_2O_5 content. Above 10 mol% of V_2O_5 a new band appears at 1027 cm^{-1}, which gradually increases in intensity with increasing V_2O_5 content. This band is related to the vibrations of isolated V=O vanadyl groups in VO_5 trigonal bipyramids [27, 28]. Dimitrov et al. [1] reported detailed data on the IR spectra of vitreous $V_2O_5{-}Bi_2O_3$ (20≤ mol% V_2O_5 ≤ 100) binary system. They have shown the appearance of one band at 930 cm^{-1} in $60V_2O_5{-}40Bi_2O_3$ glass spectrum which gradually shifts to 950 cm^{-1} in $80V_2O_5{-}20Bi_2O_3$ glass. This band is attributed to the vibrations of the free VO_2 groups of VO_4 tetrahedra, forming chains with V−O−V bridges. This suggests that the absorption band at 915 cm^{-1} in $20V_2O_5{-}30CdO{-}\ 50P_2O_5$ glass which gradually shifts to 920 cm^{-1} in $50V_2O_5{-}50P_2O_5$ glass could be related to the simultaneous vibrations of P−O−P asymmetric in pyrophosphate groups and VO_2 groups of VO_4 tetrahedra. The bands around 765 cm^{-1} are broadened in the spectra containing pyrophosphate groups (x ≥ 20 mol% V_2O_5). The broadened bands can be attributed to the coexistence of the vibrations of P−O−P bridge bonds of $P_2O_7^{4-}$ groups and the vibrations of V−O bonds of isolated VO_4 groups [29, 30].

At low frequencies, the two bands centered at 473 and 520 cm^{-1} assigned to the bending vibration of (δ) of P–O bonds decrease in intensity and transform into one band centered at 510 cm^{-1} for higher V_2O_5 content. Results show that the increasing of the V_2O_5 content over 20 mol% decreases the bending harmonics of O=P−O which being replaced with specific vibration of vanadium ions. Thus, this band can be assigned to the combined bending vibrations of V−O [31] and PO_4^{3-} groups [26]. Above x = 20 mol% V_2O_5, two weak bands appear at 569 and 630 cm^{-1} which can be attributed to the bending vibrations of V−O [28, 32-34]

The Raman spectra of $xV_2O_5{-}(50\text{-}x)CdO{-}50P_2O_5$ glasses (0 ≤ x ≤ 50 mol%), in the frequency range between 200 and 1400 cm^{-1} are shown in Fig. 4. The two most intense peaks in the spectrum of the $50CdO{-}50P_2O_5$ glass (x = 0 mol%) are due to the symmetric bridging stretching vibrations (ν_s) of the units along the chains at 696 cm^{-1}, and the terminal P–O stretching vibrations (ν_s) of the PO_2 units at 1172 cm^{-1} [33]. A second symmetric stretching P−O−P band observed at 789 cm^{-1} may be due to very short chain phosphate units or ring structures [36, 37]. The lower intensity peak at 1250 cm^{-1} is the asymmetric PO_2 stretch mode ($\nu_{as}PO_2$) and the small peak at 1065 cm^{-1} is the symmetric stretch mode PO_3 end groups (ν_sPO_3) [36]. The broad bands at 330 and 500 cm^{-1} are modes most likely involving phosphate bending motions [38]. The frequency of PO_2 asymmetric shifts to lower frequency with increasing V_2O_5 content.

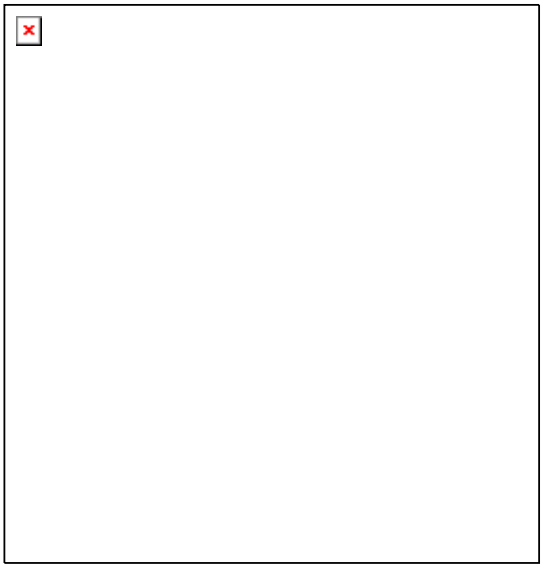

Fig. 4. Raman spectra of $xV_2O_5{-}(50\text{-}x)CdO{-}50P_2O_5$ glasses.

Upon addition of vanadium pentoxide to cadmium metaphosphate the following spectra changes are observed : the bands observed around 696 cm^{-1} and 1172 cm^{-1} disappear completely when x reaches 20 mol% and the band observed around 1250 cm^{-1} disappears for x = 50 mol%. New bands appear at 615 cm^{-1}, 760 cm^{-1}, 974 cm^{-1} and 442 cm^{-1}. The spectrum with the highest vanadium concentration studied (x = 50 mol%) shows a weaker broad band at about 442 cm^{-1}. This band is assigned to the V−O−V vibrations of metavanadates [39]. The band at 615 cm^{-1}, which appears for x ≥ 10 mol% is assigned to the formation of PO_4 tetrahedral units, bridged through one oxygen to vanadium ($V{-}O{-}PO_3$) [2]. The spectra with x ≥ 20 mol% show a broad band in the 760-750 cm^{-1} region. This band is assigned to the overlapping V−O−V bridging vibrations which arises by connecting neighboring VO_n polyhedra through oxygen in the glass [2] and P−O−P bridging vibrations in pyrophosphate groups $P_2O_7^{4-}$ [38]. The band at 974 cm^{-1} (x= 10 mol%) which shifts to 908 cm^{-1} (x = 50 mol%) can be assigned to the V=O vibrations of either tetrahedral VO_4 or trigonal bipyramidal VO_5 [3]. The band in the 1027-1024 cm^{-1} region is corresponding to

the symmetric PO_3 stretching modes of dimer $P_2O_7^{4-}$ unit [3, 38].

5. Discussion

The evolution of the glass transition temperature can be interpreted from the structural description of the network structure. The maximum in T_g can be explained by considering changes in the nature of the oxygen bonds that constitute the glass network. The increase in T_g usually means an increase of the glass rigidity. In the first composition region at low V_2O_5 concentration ($x \leq 20$ mol%) the glass has the continuous phosphate network. FTIR spectra (Fig. 3) indicate the structural changes of ternary samples with 50 mol% P_2O_5. Absorption band of (PO_2) asymmetric stretching mode shifts to lower frequencies as the V_2O_5 content increase. Since the electronegativity of V^{5+} (1,9 eV) is larger than that of Cd^{2+} (1,5 eV) [40], we expect that the vanadium−oxygen bond is more covalent than the cadmium−oxygen bond, and the phosphorus−oxygen bonds linked to vanadium ions P−O(−V) are more ionic than P−O(−Cd) bonds. Furthermore, the decrease of (PO_2) asymmetric intensity confirms that P−O−Cd bonds will be replaced by the P−O−V bonds when introducing the vanadium oxide. Absorption band of P−O−P asymmetric stretching mode shifts to higher frequencies as the V_2O_5 content increases. The band shift can be explained by an increase in the covalent fraction of P−O−P bonds, indicating that the P−O−P bonds are strengthened with the substitution of V_2O_5 for CdO [20, 35]. As a result of this, T_g increases (see Fig. 2). In the second composition region ($x \geq 20$ mol%) , the IR and Raman data show that the structure changes from the continuous phosphate network to the continuous vanadate network by the formation of either tetrahedral VO_4 or trigonal bipyramidal VO_5 with V=O bonds and short phosphate units such as $P_2O_7^{4-}$ groups. The main effect observed in IR spectroscopy, with V_2O_5 addition, is the decrease in intensity of the in-chain P−O−P asymmetric and symmetric indicating that the numbers of in-chain P−O−P bonds are diminishing with the increase of V_2O_5 content. For the higher V_2O_5 content ($x = 50$ mol%) the IR and Raman spectra show that the V−O and V−O−V vibrations are well observed, indicating that the V−O and V−O−V bonds predominate into the glass network. The V−O−V bond between the VO_4 tetrahedra is less strong than the P−O−P bond between the PO_4 tetrahedra because the bond strength (q/a) of V^v (q/a = 2.65 $Å^{-1}$) is smaller than that of P^v (q/a = 3.29 $Å^{-1}$) [40]. Thus, the decreasing of the fraction of the stronger P−O−P bonds and the increasing of the fraction of the weaker V−O−V bonds with vanadium oxide addition ($x \geq 20$ mol%) are responsible for the decrease of T_g.

6. Conclusions

The composition dependence of T_g , infrared spectroscopy and Raman spectroscopy of the xV_2O_5–(50-x)CdO–$50P_2O_5$ glass system over the compositional range $0 \leq x \leq 50$ mol% show that the rigidity of the vitreous matrix is related to the manner in which V_2O_5 gets arranged in the glass. For low vanadium oxide concentrations ($x \leq 20$ mol%), FTIR and Raman spectra reveal the formation of P−O−V bonds, which increase the cross-link strength of the glass network and leads to increased T_g. In the high V_2O_5 concentration range ($x > 20$ mol%), the vanadium oxide plays the role of a second glass former and it is evolved from a phosphate network to a vanadophosphate network where pyrophosphate groups $(P_2O_7)^{4-}$ can be detected. The vanadium takes part in the network of the glasses as VO_5 and VO_4 groups forming chains with V−O−V bridges. The increasing of the fraction of the weaker V−O−V bonds and the diminishing of the numbers of the stronger in-chain P−O−P bonds with the increase of V_2O_5 concentration decrease the glass network connectivity, in accordance with the decrease of T_g.

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