Structural studies of binary iron vanadate glass

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Abstract

Structural studies of iron vanadate glasses were carried out using differential thermal analysis, infrared (IR) and Mössbauer spectroscopy. Glasses with cross-linking density higher than the vitreous V_2O_5 were obtained by introducing Fe_2O_3 in the V_2O_5 matrix. Mössbauer spectra are consistent with an interpretation in which iron ions exist as Fe^{3+} with tetrahedral coordination in the glass compositions. IR spectra indicate that Fe^{3+} ions occupy substitutional positions in all glass compositions, without affecting the V=O bond vibration.

1. Introduction

By contrast with the variety of studies performed on the physical properties of the semiconducting vanadate glasses, only a few studies have so far been reported on the structure of these glasses [1–10]. Structural studies of the crystalline and vitreous V_2O_5 reveal [1,11–13] that each V^{5+} ion is surrounded by five oxygen atoms making a distorted tetragonal pyramid, which can also be viewed as a distorted trigonal bipyramid sharing edges and corners to form layers. Infrared (IR) studies of several binary vanadate glasses [1,6–10] show that the network-formers such as SiO_2, GeO_2, etc., affect no significant structural changes of the vitreous V_2O_5 network, while the network modifiers such as alkali or alkaline earth oxides destroy the vanadate layers followed by the

formation of tetrahedral VO_4 units. Neutron diffraction studies [14] indicate that the coordination number of vanadium is always five in phosphorous, barium or lead vanadate glasses irrespective of the glass composition. Mössbauer spectroscopy has also been used for the structural studies of ternary vanadate glasses containing Fe_2O_3 [15–18]. On the basis of the Mössbauer parameters, the coordination number of Fe^{3+} ions is reported to be either four or six or both in the ternary alkali and alkaline earth vanadate glasses [15–18]. The purpose of this paper is to study the structure of the binary iron vanadate glass compositions using differential thermal analysis (DTA), Mössbauer and infrared spectroscopy.

2. Experimental procedure

Glass samples of compositions $(V_2O_5)_{100-x}$-$(Fe_2O_3)_x$ with $x = 5$–20 mol% were prepared from reagent-grade V_2O_5 and Fe_2O_3. The mixtures of these chemicals were melted at 1200°C in covered alumina crucibles for 1 h in an electrical furnace and

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the melts were quenched by pouring onto a twin roller. The atomic absorption spectroscopic analysis showed that the final glass compositions did not differ much (0.06 mol%) from the batch compositions. The amorphous nature of the samples was confirmed by X-ray diffraction studies. The DTA measurements of the samples were performed in a thermal analyser (Shimadzu DT-30) with a heating rate of 20°C/min in the temperature range 30–600°C. The IR spectra at room temperature of the powdered glass samples in the KBr matrix were recorded in a spectrometer (Perkin–Elmer, model 783) in the wave number range 200–4000 cm^{-1}. Mössbauer spectra of the samples at room temperature were taken in a standard spectrometer (Wissel) operating in the constant-acceleration mode. A 5 mCi ^{57}Co in Rh matrix is used as a source. High-purity 25 μm natural Fe foil (supplied by Amersham International) was used to calibrate the channels.

3. Results

3.1. DTA study

Fig. 1 shows a typical DTA curve for a glass composition. The curve consists of an endothermic peak due to a glass transition and an exothermic peak due to crystallization. The DTA curves of other glass compositions are similar to that presented in
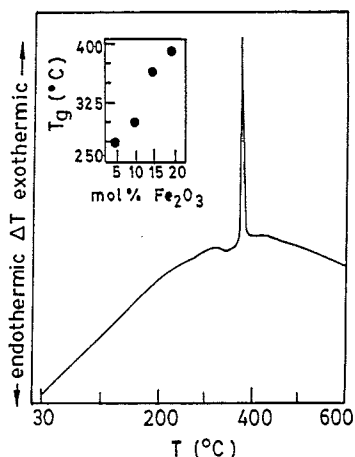
Fig. 1. Differential thermal analysis curve for 90 V_2O_5–10 Fe_2O_3 glass composition. The inset shows the compositional dependence of the glass transition temperature.
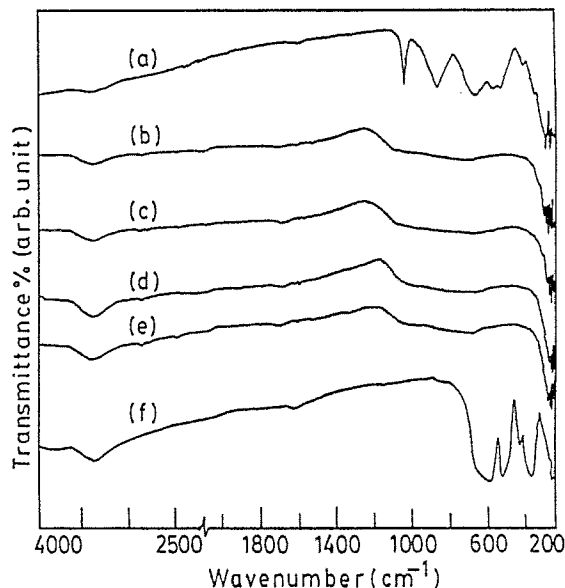
Fig. 2. Room-temperature infrared spectra of iron vanadate glasses and starting materials: (a) crystalline V_2O_5, (b) 95 mol% V_2O_5, (c) 90 mol% V_2O_5, (d) 85 mol% V_2O_5, (e) 80 mol% V_2O_5, (f) crystalline Fe_2O_3.

Fig. 1. The compositional dependence of the glass transition temperature, T_g, is shown in the inset of Fig. 1, indicating the increase of T_g with an increase of Fe_2O_3 content in the glass compositions. It may be noted that the T_g of these glasses are higher than that (T_g = 216°C) of vitreous V_2O_5 [19].

3.2. IR spectroscopic study

The IR spectra of the glass compositions are shown in Fig. 2 along with those of crystalline V_2O_5 and Fe_2O_3. The spectrum for crystalline V_2O_5 shows the presence of absorption bands at ~ 1020, ~ 830, ~ 620, ~ 480 and ~ 380 cm^{-1}, which is consistent with the results reported earlier [1]. For the glass compositions, the band at 1020 cm^{-1} becomes a very weak shoulder and there is no shift of this band with the increase of Fe_2O_3 content in the glass compositions. The intensities of the other bands of crystalline V_2O_5 decrease and broaden significantly in the glass compositions owing to their disordered structures. There is no evidence in the IR spectra for the presence of characteristic bands of Fe_2O_3. It may be noted that a band at 3400 cm^{-1} is observed in the spectra of all glass compositions and crystalline V_2O_5
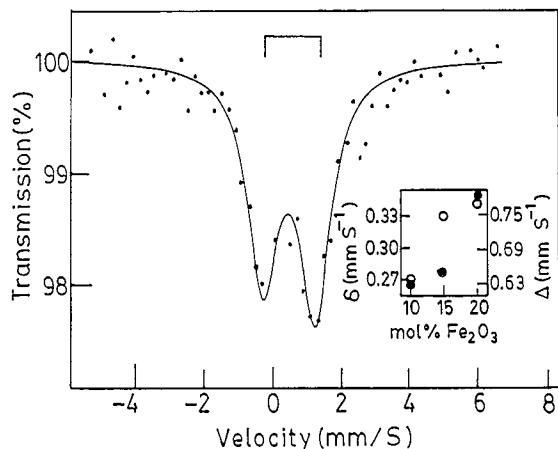
Fig. 3. Mössbauer spectrum of 80 V_2O_5–20 Fe_2O_3 glass composition. The inset shows the compositional dependence of the isomer shifts (O) and quadrupole splittings (●).

and Fe_2O_3 due to adsorbed water in the powdered samples.

3.3. Mössbauer study

Fig. 3 shows a Mössbauer spectrum of a typical glass composition. The spectrum consists of two lines with a large linewidth and asymmetry which is expected due to the variation of local surroundings of Fe ions in the glassy matrix. The spectra of the other compositions exhibited a similar appearance. The spectra show no hyperfine splitting, indicating that the iron ions are randomly distributed in the glass compositions. The spectra were fitted with a sum of two Lorentzian peaks of one paramagnetic doublet, giving a good χ^2 value. The Mössbauer parameters, i.e., isomer shifts, δ, quadrupole splittings, Δ, and linewidths, Γ, were obtained from the fittings within a maximum error of ± 0.03 mm s^{-1}

Table 1
Mössbauer parameters of some iron vanadate glass compositions

Glass compositions (mol%)		Isomer shift (± 0.03 mm s^{-1})	Quadrupole splitting (± 0.03 mm s^{-1})	Linewidth (± 0.03 mm s^{-1})
V_2O_5	Fe_2O_3			
90	10	0.27	0.63	0.42
85	15	0.33	0.64	0.44
80	20	0.34	0.78	0.53

and are shown in Table 1. The variation of the isomer shifts and quadrupole splitting with glass composition is shown in the inset of Fig. 1. Both the isomer shifts and quadrupole splittings increase with an increase of Fe_2O_3 content in the glass composition.

4. Discussion

On the basis of the DTA studies on the structure of oxide glasses, it has been reported [20,21] that T_g is strictly related to the density of cross-linking, the tightness of packing in the network, the coordination of the network-formers, etc. It has been also suggested [20] that the density of cross-linking and the molar oxygen volume in the oxide glasses have greater effects on T_g than the bond strength. The increase of T_g with glass composition is thus due to the higher cross-linking density in the iron vanadate glasses than in the vitreous V_2O_5. As the Fe_2O_3 content increases, there is a continuous change of the glass matrix from a 2D layer structure into a more complicated 3D structure. Our earlier studies [7] also indicated that the oxygen molar volume in these glasses increased with an increase of Fe_2O_3 content in the glass composition, supporting this conclusion.

The IR spectra of the crystalline and amorphous V_2O_5 have been reported earlier [1,22]. The IR band at ~ 1020 cm^{-1} of crystalline V_2O_5 is characteristic of the isolated V=O bond [1]. The bands at ~ 830 and ~ 620 cm^{-1} are due to the symmetric and antisymmetric vibrational modes of the V–O–V group and the band at ~ 480 cm^{-1} is attributed to the angular deformation vibration of the O–V bond [19]. The IR spectra of amorphous V_2O_5 also show these absorption bands at the same wave numbers but are broadened due to short-range order [22]. It has been reported [1] that the IR characteristic of the vanadium–oxygen bond of crystalline and amorphous V_2O_5 are also maintained in several vanadate glasses. The occurrence of the V=O bond vibration in the glass compositions at nearly the same position (1020 cm^{-1}) can be understood from the distribution of the Fe^{3+} ions in the structure of the glasses. When Fe_2O_3 is introduced into the V_2O_5 matrix, two different forms of Fe^{3+} ion distribution in the structure of the glasses have been suggested in relation to

vanadium–oxygen polyhedra: interstitial sites and substitutional sites [1]. This would influence the isolated $V=O$ bond and thus affect the vibrations of the $V=O$ bond depending upon the position of the Fe^{3+} ions. In the first case, the Fe^{3+} ions are located between the vanadate chains and layers. They can interact directly with the isolated $V=O$ bonds and, consequently, the bonds will be longer and the frequencies of vibrations should be shifted towards lower wave number. In this case, the formation of a series of complexes with more than one $V=O$ bond, having vibrational frequencies close to each other [1], would result. As these overlapping bands cannot be resolved, a broad maximum should be observed which shifts to lower wave numbers with increase of Fe_2O_3 in the V_2O_5 matrix due to the destruction of the vanadate layers. In the second case, Fe^{3+} ions occupy positions in the chain itself, where some of the weaker $V-O-V$ bonds break and they form new $V-O-Fe$ bridges. Thus the influence of the Fe^{3+} ions on the $V=O$ bond in the glass structure is restricted and it may have an indirect manifestation making no significant change in the position of the $V=O$ bond vibration. Thus in the present glass composition, for which no significant change of the $V=O$ bond vibration has been observed, the Fe^{3+} ions occupy substitutional positions. This result is in sharp contrast with the results reported earlier [1] for some vanadate glasses containing iron ions. The difference might be due to the different conditions of glass preparation (melting temperature, duration of melting, etc.).

It has been suggested in the literature [23–25] that the values of the isomer shifts and quadrupole splittings can be used to infer the coordination and valence state of iron ions in glasses. The isomer shifts for tetrahedrally coordinated Fe^{3+} ions are generally lower than about 0.4 mm s^{-1}, while the octahedrally coordinated Fe^{3+} ions have isomer shifts higher than 0.4 mm s^{-1}. The Fe^{2+} ions have much higher isomer shifts and quadrupole splittings than the Fe^{3+} ions. It is therefore concluded from the values of the isomer shifts (Table 1) that the doublet observed in the present glass compositions is due to tetrahedrally coordinated Fe^{3+} ions and thus the Fe^{3+} ions occupy substitutional positions as FeO_4 tetrahedra, which is consistent with the IR spectra. The increase of quadrupole splittings with Fe_2O_3

content in the glass composition results from the smaller 4s electron density of Fe^{3+} ions and the higher asymmetry of the FeO_4 tetrahedra with higher Fe_2O_3 content, and thus the covalency of the $Fe^{3+}-O$ bond decreases in the glass compositions with an increase of Fe_2O_3 content [26].

5. Conclusions

In the iron vanadate glass compositions, the iron exists as Fe^{3+} ions with tetrahedral coordination occupying substitutional positions interacting indirectly with the $V=O$ bond and thus making no significant changes in the $V=O$ band position. Introduction of Fe_2O_3 into the V_2O_5 matrix changes the 2D layer structure of crystalline V_2O_5 into a more complicated 3D structure.

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