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Thermodynamics of oxidation-reduction of vanadium in borate glasses

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The $V^{4+} \leftrightarrow V^{5+}$ equilibrium in a $2BaO-3B_2O_3$ glass has been studied as functions of temperature, at a fixed partial pressure of oxygen, and total vanadium concentration of the melt. The optical and esr spectra of some of these glasses have also been studied to characterize the V^{4+} and V^{5+} centres. From the linear temperature dependence of the redox concentration ratio, the activation energy for the redox reaction has been determined at each concentration. The plot of logarithm of the ratio of the activity coefficients and also of the enthalpy of the redox reaction against composition showed considerable changes around 22 mol % V_2O_5. Structural changes associated with both V^{4+} and V^{5+} ions are suggested to account for such behaviour, which was also suggested from a previous study of the conductivity behaviour of such glasses. The optical and esr spectra showed considerable changes in the V^{4+}– O and V^{5+}– O bonding, but no sudden change was observed around 22 mol % V_2O_5.

1. Introduction

During the last decade, a considerable amount of work has been done on semiconducting oxide glasses containing different transition metal (TM) ions. The conductivity in such glasses arises due to hopping of electrons between two different oxidation states of the TM ions. Therefore, the study of oxidation–reduction behaviour of TM ions is very important. This is also important for understanding the nature of colour in coloured glasses, for which most of the efforts were diverted during the past years. This kind of study is more relevant for cases where conductivity was studied as a function of redox ratio [1–4]; this has been done without a prior knowledge of the oxidation–reduction behaviour of the TM ions in the glasses studied.

Although iron has been used in many cases, vanadium was mostly used with phosphate in producing semiconducting glasses. The study of oxidation–reduction behaviour becomes more complicated in cases where more than two oxidation states of the transition metal are present in glass, e.g. in vanadium phosphate glasses the occurrence of V^{3+}, V^{4+} and V^{5+} is fairly common. Therefore, a barium borate glass, which stabilizes the higher oxidation state of vanadium more than the phosphate glass [5], was chosen for this work. In the present work, the V^{4+}–V^{5+} equilibrium was studied in atmospheric oxygen at different temperatures. The results on the measurements of optical and esr spectra are also presented to derive information about the valence states, co-ordination and co-valency of vanadium.

2. Experimental details

Five different series of glasses were melted in the $BaO-B_2O_3-V_2O_5$ system having V_2O_5 content of 10.5, 16.8, 22.6, 26.1 and 33.6 mol %, respectively, while the $BaO:B_2O_3$ ratio was kept constant at 2:3. The batch materials were analar grades of $BaCO_3$, anhydrous B_2O_3 and pure V_2O_5. The batch for producing 10 g glass was thoroughly mixed and melted in a platinum crucible for 8 h. The melting temperature varied between 980 and 1320° C; six glasses were melted in each series at six different temperatures. Air ($10\,ml\,min^{-1}$) was bubbled through the melt for

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at least 7 h in order to homogenize the melt and to attain equilibrium, between the different valance states of vanadium, with respect to a constant p_{O_2} at every temperature. All the glasses were air-quenched except for five glasses (one from each series) melted at the highest temperature. These five glasses were annealed at temperatures in the range 450 to 250° C, depending on the concentration of V_2O_5, because they were to be used for optical and esr measurements.

All the samples were chemically analysed for total V and V^{4+}, assuming that vanadium was present in the glasses only as V^{5+} and V^{4+} ions, as it was confirmed by the measurements of the optical spectra. The glasses were dissolved in aqueous solution in the absence of any oxidizing or reducing agents, thus the actual V^{4+}/V_{total} ratio was preserved. Therefore, V^{4+} was estimated by dissolving 1.0 g finely powdered glass in 50 ml 6 N aqueous HCl and measuring the optical density at 760 mm. The total V was estimated by reducing all the vanadium ions in the solution to V^{4+} and repeating the optical density measurement; V^{5+} was determined from the difference in optical densities. The amounts of V_2O_5 and VO_2 were calculated by comparing the optical densities with a known standard.

The optical spectra were measured by a Cary 14 spectrophotometer from 5 000 to 25 000 cm^{-1} on polished specimens. The slabs were then crushed and used for esr measurement.

The esr spectra were recorded at room temperature on a Hilger and Watts microspin spectrometer operated at X-band frequency with a magnetic field modulation frequency of 100 kHz. The magnetic field was calibrated using a proton resonance probe, and it was swept at approximately 50 G min^{-1}; 1 G field markers were placed on the spectra at approximately 60 G intervals. The coarsely powdered glass sample, contained in a quartz tube, was introduced into the resonance cavity operating in the $H_{0\,1\,1}$ mode. The sample weight (about 0.2 g) and the other experimental conditions were kept identical to make the results of these glasses comparable to each other.

Some of these glasses were tested by X-ray diffration and transmission electron microscopic techniques to detect the presence of any crystalline phase or any liquid–liquid phase separation. None of these glasses showed any crystal diffraction peaks. From the electron micrographs, no sign of phase separation could be seen in any of the as-annealed or non-annealed glasses. Therefore, it was concluded that none of the glasses studied were either crystallized or phase separated.

3. Results and discussion

3.1. Oxidation–reduction behaviour of $V^{4+} \leftrightarrow V^{5+}$

Generally, oxidation–reduction equilibrium of any transition metal oxide in glass depends upon (a) standard free energy of the reaction concerned, (b) partial pressure of oxygen, and (c) activity of the component oxides in the glass. All these factors are again dependent on temperature.

In the case of the reaction

$$4\,VO_2\ (\text{solid}) + O_2\ (\text{gas}) \overset{K_T}{\rightleftharpoons} 2\,V_2O_5\ (\text{liquid}), \quad (1)$$

the standard free energy of the oxidation reaction is $\Delta G^{O}_{T} = -20\,119.3 + 9.6\,T$ J (mol oxygen)$^{-1}$ [6]. With increasing temperature, the free energy change of the above reaction becomes less negative, thus with a constant oxygen potential (p_{O_2} = air) the redox distribution will move towards the reduced side with increasing temperature. From the standard free energy change of Equation 1, the value of equilibrium constant can be calculated, because $\Delta G^{O}_{T} = -RT \ln K_T$.

If this vanadium–oxygen system is now dissolved in a $BaO–B_2O_3$ glass melt, Equation 1 can be written as

$$4\,VO_2\ (\text{glass}) + O_2\ (\text{glass}) \overset{K_T}{\rightleftharpoons} 2\,V_2O_5\ (\text{glass}), \quad (2)$$

from which

$$K_T = \frac{(a_{V_2O_5})^2_{\text{glass}}}{(a_{VO_2})^4_{\text{glass}}} \cdot \frac{1}{(p_{O_2})_{\text{glass}}}, \quad (3)$$

where a_i indicates the activity of the ith oxide and under equilibrium condition, p_{O_2} (glass) = p_{O_2} (furnace atmosphere). In this investigation, glasses were melted with a small amount of V_2O_5 ($\leqslant 33.6$ mol %); the melts were not saturated and thus were not in equilibrium with either V_2O_5 (liquid) or VO_2 (solid). In such a non-standard state Equation 3 can be written as

$$K_T = \frac{C^2_{V_2O_5}}{C^4_{VO_2}} \cdot \frac{\gamma^2_{V_2O_5}}{\gamma^4_{VO_2}} \cdot 1/p_{O_2} \quad (4)$$

$$\text{or } K_T = \frac{C^2_{V_2O_5}}{C^4_{VO_2}} \cdot \beta \cdot 1/p_{O_2} \quad (5)$$

where C_i and γ_i are the mole fraction and the activity coefficient, respectively, of the ith oxide in the glass. Equation 4 indicates that $a_i \neq C_i$, because the activity coefficients are not unity in our case [5].

Although the activity coefficients of the individual oxides cannot be calculated from Equation 4, their ratio (β) can be calculated as a function of concentration of total vanadium at a particular temperature, since the values of $C_{V_2O_5}$ and C_{VO_2} are known from the chemical analysis data, and the values of K_T can be extracted from the standard thermochemical data. In Fig. 1, log β at 1320° C is plotted against mol% V_2O_5. This shows a dispersion type of behaviour with a significant change around 22 mol% V_2O_5. This change could be ascribed to either changes of ${}^{\gamma}V_2O_5$ and/or ${}^{\gamma}VO_2$ in the melt. At least, it can be suggested that there is a major change in the pattern of interaction between vanadium oxides and glass melt around 22 mol % V_2O_5. This type of dispersion behaviour of log β is not usual in some other redox systems [7]. However, a considerable change of log β with mol % V_2O_5 has been noted in the barium alumino-borate system [5], but at a much lower value of 6 mol %. It should be mentioned that Fig. 1 could be drawn in other ways, but a dotted line was drawn to show the variation, instead of drawing a straight line with the 1st, 2nd and the 5th points, in which case the 3rd and 4th points would lie above and below the straight line; the confidence limit (95%) for log β is ± 0.1 in Fig. 1. It should be pointed out that the apparent molar volume showed a change of slope around 22 mol % V_2O_5 in this system [8]. This was ascribed to changes in the co-valency of the V^{4+}–O and V^{5+}–O bonding. From our esr results we have also observed a considerable change in the electronic structure of V^{4+}, but no sudden change was observed around 22 mol % V_2O_5. Paul and Yee [5] observed a change of V^{5+}–O bonding in a barium alumino-borate glass.

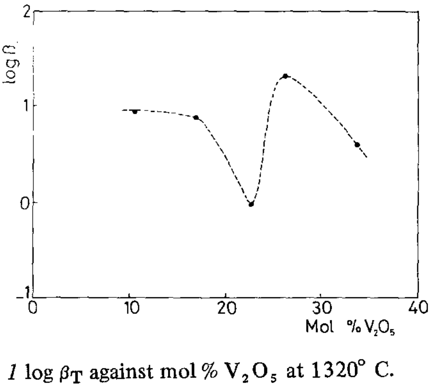

Figure 1 log β_T against mol % V_2O_5 at 1320° C.

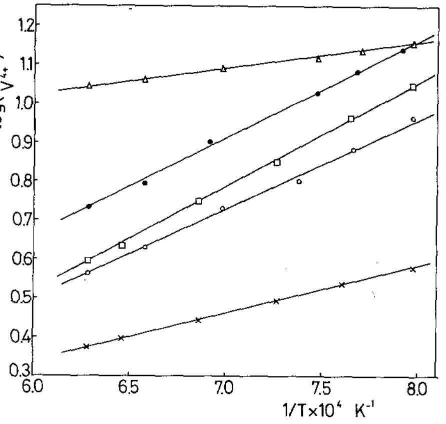

Figure 2 Log (V^{5+}/V^{4+}) against $1/T$ for five different series of glasses. ⊙ Series 1 (~ 10.5 mol % V_2O_5), ⊡ series 2 (~ 16.8 mol % V_2O_5) , △ series 3 (~ 22.6 mol % V_2O_5), X series 4 (~ 26.1 mol % V_2O_5), ● series 5 (~ 33.6 mol % V_2O_5).

In principle, the equilibrium condition (Equation 3) can also be represented by the relation [5]

$$4V^{4+}(\text{glass}) + O_2(\text{glass}) \rightleftharpoons 4\,V^{5+}\,(\text{glass}) + 2\,O^{-2}\,(\text{glass}). \qquad (6)$$

Over a limited temperature range, as in the present case (980 to 1320° C), the activity of O^{-2} remains practically constant for a melt of constant chemical composition, and p_{O_2} = air. Therefore, from Equation 6

$$4 \log (V^{5+}/V^{4+}) = \log K_c + \text{constant}, \qquad (7)$$

where K_c is the concentration equilibrium constant. From Van't Hoff Isochore

$$\log K_c = -\left(\frac{\Delta H}{2.303\,RT}\right) + \text{constant}, \qquad (8)$$

where ΔH is the enthalpy of Reaction 6. Combining Equations 7 and 8

$$\log (V^{5+}/V^{4+}) = -\left(\frac{\Delta H}{9.212\,RT}\right) + \text{constant}. (9)$$

Thus a plot of log (V^{5+}/V^{4+}) against $1/T$ is expected to be linear. Such plots for the five series of glasses are shown in Fig. 2. It should be noted that the ratio of the activity coefficients of V^{4+} and V^{5+} is evidently assumed to be constant, as in reference [5]. Even if the individual activity coefficients change with temperature, their ratio might not change significantly keeping the variation of

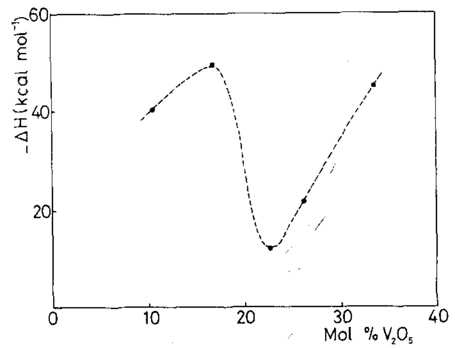

Figure 3 The activation enthalpy (ΔH) against mol % V_2O_5.

log (V^{5+}/V^{4+}) against $1/T$ linear, as shown in Fig. 2, which justifies the above assumption.

The values of ΔH, calculated from the slopes of Fig. 2, are plotted against mol % V_2O_5 in Fig. 3. The confidence limit (95%) for ΔH is ± 1.5 kcal mol^{-1} in Fig. 3, which is almost covered by full circles in this figure. It is again seen that the interaction pattern between vanadium oxides and glass melt changes considerably around 22 mol % V_2O_5. As in the case of the variation of log β, ΔH also shows a very unusual variation with composition. This is only evident when a system is studied with a wide range of composition, because almost all the previous studies were confined to a low concentration regime. It shoud be mentioned that the maximum around 15 mol % V_2O_5 is thought to be insignificant in comparison with a deep minimum around 22 mol % V_2O_5, where the conductivity parameters and the apparent molar volume showed considerable changes [8].

3.2. Optical spectra

The optical spectra of these glasses were identical to those shown in [8]. Two broad bands were observed at around 10 000 and 17 000 cm^{-1}, respectively, which are ascribed to $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow b_1^*$ transitions respectively. A steep rise of optical density at high wavenumbers was ascribed to V^{5+}; the height and position of this absorption tail showed a considerable variation with increasing total V_2O_5. This could be ascribed to a change of V^{5+}–O bonding [5], which is reflected in the redox equilibrium of this system. No sign of V^{3+} was observed even when the spectra were analysed in a Du pont 310 curve resolver assuming a Gaussian function. The details of the band analysis are given in [8].

3.3. Esr spectra

The esr spectra of these glasses were very similar to those obtained in the previous work [8]. The spectra were analysed by an axial spin Hamiltonian, and the esr parameters were calculated by a computer-fitting procedure as described before [8] and are shown in Table I. The main difference is that these glasses contain much higher V^{4+} than those studied previously. However, there is not a significant difference between the calculated esr parameters of these glasses with those of the previous study [8]. It is seen from Table I that, while $g_\perp$ increases a little with increasing V_2O_5, $g_\parallel$ shows a considerable decrease; while $A_\perp$ increases smoothly with increasing V_2O_5, $A_\parallel$ shows a maximum around 22 mol % V_2O_5 suggesting a structural change of V^{4+} at this composition. However, the anisotropic contributions of the $3d_{xy}$ electron to the hyperfine splittings (both $A'_\perp$ and $A'_\parallel$) decrease considerably with increasing V_2O_5. These results show that the co-valency of the V^{4+}–O bonding increases considerably as the vanadium content increases, but no sudden change was observed around 22 mol % V_2O_5.

4. Conclusions

The oxidation–reduction behaviour of $V^{4+} - V^{5+}$ in a BaO–B_2O_3 glass shows a considerable change in the interaction pattern between vanadium oxides and glass melt around 22 mol % V_2O_5. This could be due to the structural changes associated with both V^{4+} and V^{5+} ions, which was also sug-

TABLE I The esr parameters of the glasses

Glass No*	V_2O_5 (mol%)	V^{4+}(%)	$g_\perp$	$g_\parallel$	$\lvert A_\perp \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A_\parallel \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A'_\perp \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A'_\parallel \rvert$ ($\times 10^4$ cm^{-1})
3F	10.5	21.4	1.9670	1.9350	58.40	165.4	29.30	78.50
6F	16.8	20.2	1.9685	1.9293	59.04	166.3	28.99	78.28
9F	22.6	8.3	1.9695	1.9180	59.40	166.9	28.40	77.10
12F	26.1	29.7	1.9709	1.9140	59.70	165.2	28.00	75.90
18F	33.6	15.6	1.9720	1.9100	59.98	163.2	27.20	74.80

*These Glasses were melted at the highest temperature of melting (i.e. at 1320° C) gested from a previous study of the conductivity behaviour of such glasses. The measurements of the optical and esr spectra show that there are changes associated with V^{4+} and V^{5+} ions, but no sudden change is observed around 22 mol % V_2O_5.

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