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Effect of annealing on the electrical and optical properties of V_2O_5–GeO_2 glasses

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Increases in the electrical conductivities of vanadium germanate glasses on annealing have been reported recently in the literature. The increases were attributed to the formation of microstructure on annealing. In the present work we report a study of the V_2O_5–GeO_2 glass system using electron paramagnetic resonance, optical absorption, differential scanning calorimetry and electron diffraction techniques. The V_2O_5–GeO_2 glass system consists of an equimolar mixture of vanadium pentoxide and germanium dioxide. One sample was unannealed and the other was annealed at 300° C for about 24 h.

The results revealed that the increase in the electrical conductivity of the annealed samples could be attributed to the increase of reduced valence states of vanadium ions which accompany the microstructure formation and not solely to the structural change.

1. Introduction

For vanadium germanate glasses the electrical conductivity measured by Chung and Mackenzie [1] was much smaller than that measured by Rao [2], as was pointed by Chung and Mackenzie. Recently, Khan *et al.* [3] have measured the electrical conductivity of annealed and unannealed vanadium germanate glasses. These measurements clearly elaborated the discrepancies between the two results. The conductivity of annealed samples at room temperature was found to be about 5 orders of magnitude greater than that of the unannealed samples containing a similar amount of vanadium oxide. The increase in conductivity on annealing was attributed by Khan *et al.* to the change in microstructure of the glasses.

The general condition for semiconducting behaviour is that the transition metal ion should be capable of existing in more than one valency state, so that conduction occurs by the movement of carriers from the lower valence state to the higher valence state. It has been established that the electrical conductivity of vanadium glasses depends upon the existence of vanadium in different valency states [4–7] and it is accepted that these materials are electronic conductors in which the transport mechanism involves the exchange of electrons between V^{4+} and V^{5+} ions. The electrical conductivities [8] of both single-crystal and molten V_2O_5 indicate that the compound is an oxygen-deficient semiconductor in which oxygen deficiency is compensated by reduction of some vanadium ions to lower oxidation states [9]. The four principal oxides of vanadium are V_2O_5, V_2O_4, V_2O_3 and VO in which the vanadium ions exist in four oxidation states +5, +4, +3 and +2, respectively.

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The purpose of the present investigation was to find whether the structural change on annealing [3] of the vanadate glass was accompanied by a change in valence states of vanadium ions. To achieve our goal, 50 mol % V_2O_5/GeO_2 glass was studied by the methods of electron microscopy, differential scanning calorimetry (DSC), electron paramagnetic resonance (EPR), and optical absorption spectroscopy.

2. Experimental procedure

50 mol % of analytical reagent grade vanadium pentoxide and germanium dioxide were carefully mixed in an alumina crucible and placed in a furnace maintained at 300° C for 1 h. This initial heating served to minimize material volatilization. The crucible was then transferred to a melting furnace maintained at a selected temperature of 1100° C and left for 3 h with frequent stirring. The homogenized melts were then cast onto a steel plate mould (pre-heated to 300° C). The samples to be annealed were transferred to an annealing furnace maintained at 300° C for two hours and were then allowed to cool slowly. The samples were disc-shaped with diameter of 3 cm and thickness of about 2 mm.

Thin glass films, which are necessary for optical examination, were obtained by a blowing technique. It is essential for the batch glass to reach a proper viscosity before these thin glass films can be blown, and this requires a careful selection of the melting temperature. The as-blown glass film was mounted onto a specially designed machinable glass ceramic specimen holder which could be placed directly into an annealing furnace as well as a spectrophotometer.

The diffraction analysis of both annealed (AN) and unannealed (UN) samples was made using a Jeol JSEM-200 transmission electron microscope. The specimen was placed on a side-entry specimen holder for the electron microscope. Since the high intensity of the electron beam of the microscope caused evaporation of our specimen, we had to change the idea of having the thin glass film as one piece. The specimen was then crushed in a clean mortar containing a small amount of acetone. Thin sections of the specimen are picked up from the surface of the liquid on a copper support grid held in a pair of fine tweezers. The grid was placed on the side-entry specimen holder and the latter placed in position. Thus the diffraction patterns were obtained.

The thermal stability of the glass was studied in a Mettler TA 3000 thermal analysis system. The differential scanning calorimetry (DSC) technique was applied where the heat flow to the sample is measured in thermally controlled conditions. The (UN) sample was well ground into a powder and contained in an aluminium crucible for measurement. The DSC pattern was then measured relative to an empty aluminium crucible which served as a reference.

The optical density of the samples was measured as a function of wavelength using a Varian DMS 90 spectrophotometer in the spectral range from 400 to 900 nm. Thin blown films of the (UN) glass were mounted on specially designed machinable glass ceramic holder. The holder could be fitted directly to the specimen mount in the spectrophotometer and also be placed in a furnace so that the specimen could be annealed. Measurement was made from the (UN) sample and then the same sample was annealed in a furnace at 300° C for 24 h. Then the measurement was repeated for the (AN) sample. In this way, the effects of the specimen thickness on the optical density were eliminated.

Powdered glass samples for EPR measurements were prepared in 3 mm internal diameter by 4 mm outside diameter Pyrex tubes. Typical samples contained approximately 350 mg and had a length of 19 mm. The whole sample was inside the active region of the EPR cavity. The insert dewar of the Varian E-257 variable temperature set was used to increase sensitivity for the room temperature measurement, and a liquid nitrogen cold finger purchased from Wilmad Glass Co, Buena, New Jersey, USA, was used for the measurement at 77 K.

The EPR spectra of the unannealed and the annealed glasses were measured at room temperature (22.3° C) and liquid nitrogen temperature (77 K) in a Varian E-109 EPR spectrometer interfaced with E-935 data acquisition system at the *x*-band frequency (9.1 GHz). The modulation amplitude and the modulation frequency employed were 5 G and 100 kHz, respectively. Both microwave power and modulation amplitude were verified experimentally to be at least five times below the onset of broadening. The spectra were centered in a magnetic field of 3.306 G and had a scan range of 2000 G.

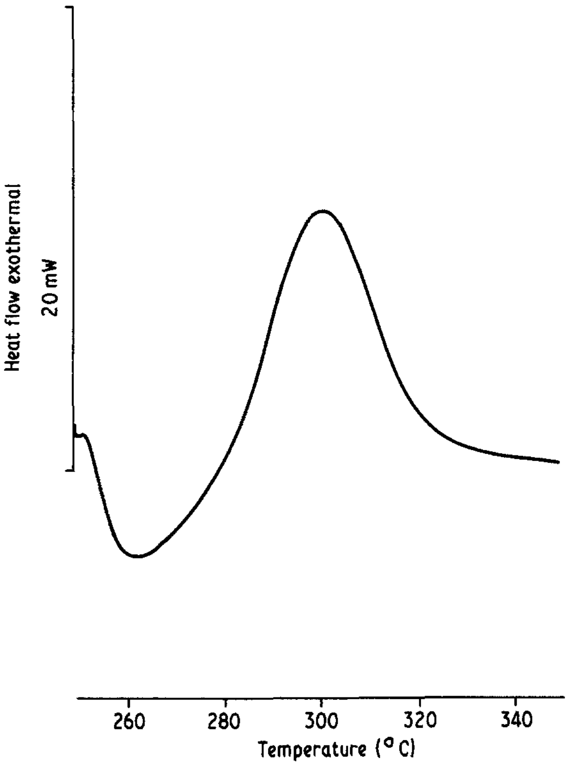

Figure 1 DSC spectrum of an unannealed sample taken at a heating rate of 25° C min^{-1}.

Magnetic field sweep was calibrated with a Varian E-500-2 self-tracking NMR gaussmeter. Microwave frequencies were mesaured with a Hewlett- Packard 5342A microwave frequency counter. Spectra were all signal-averaged 4 times to increase the signal to noise ratio. Recorded spectra were digitized to 2048 points and stored on cassette tapes for later analysis. Double integration of the first derivative curves was performed to obtain the spectral intensity. V^{4+} concentration was determined by comparison with the $CuSO_4 \cdot H_2O$ standard. The copper sulphate monohydrate was obtained from baking $CuSO_4 \cdot 5H_2O$ at 120° C overnight.

3. Results

Electron micrographs for the (AN) sample showed halos superimposed on the single crystal spot pattern, while those for the (UN) sample showed halos without the spot pattern. This suggested that the (UN) sample was non-crystalline and the (AN) sample was polycrystalline.

The DSC patterns were obtained for different heating rates, ranging from 0.4 to 40 K min^{-1}. Fig. 1 shows a DSC pattern for the heating rate of 25 K min^{-1}. It was found that exothermal peak for the phase transition in the sample structure depended on the heating rate. The transition temperature against heating rate is plotted in Fig. 2. No significant change in the weight of the sample was observed during the phase-transition as this was checked by accurate weighing of the sample before and after measurement. When the sample was cooled down to room temperature the DSC curve was re-measured and no peak appeared this time. This indicated that the phase-transition, obtained in the first measurement was permanent and irreversible.

Fig. 3 shows plots of optical density against wavelength for both the (UN) and (AN) samples. The measurements are for the same sample, made before and after annealing. It is clear from the figure that the absorption increased on annealing. It may be mentioned that the (UN) films were greenish yellow in colour while the (AN) films were dark brown.

The EPR spectrum of the (UN) sample (Fig. 4) shows the typical hyperfine structures of a 3d

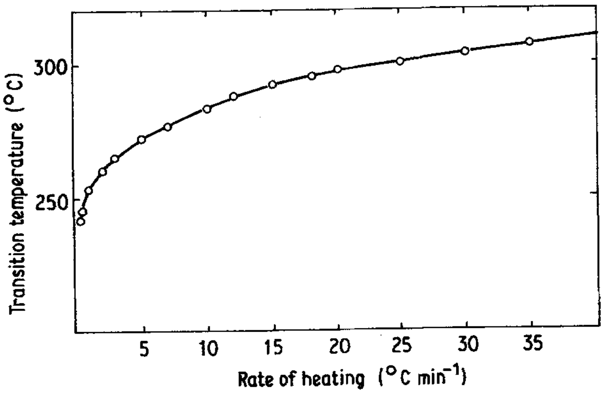

Figure 2 Dependence of the exothermal peak (Fig. 1), corresponding to the phase change, on the heating rate.

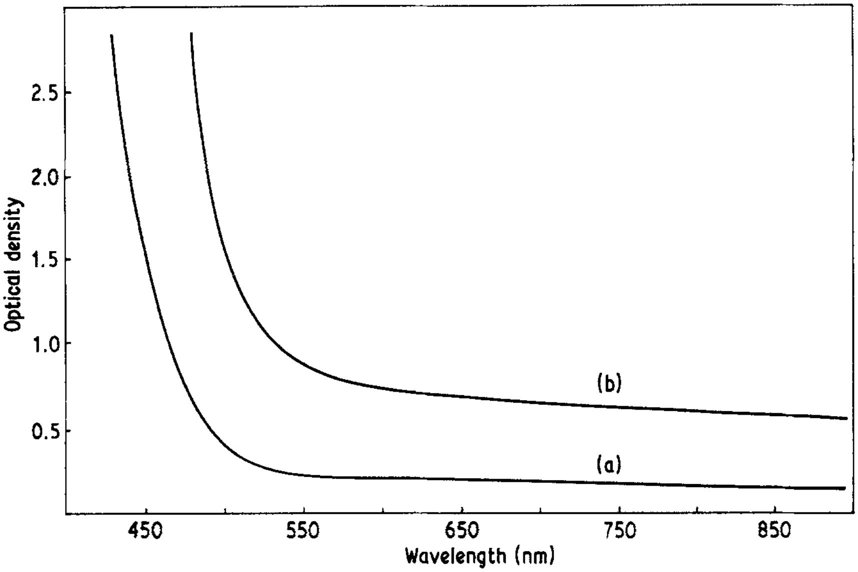

Figure 3 Room temperature optical absorption spectra of blown film, (a) before annealing and (b) after annealing.

unpaired electron localized on a single vanadium 51 nucleus of spin 7/2 [10–12]. The parallel and perpendicular feature of the *g* and hyperfine tensors seen in the spectrum suggest that the V^{4+} ion lies in an axially distorted crystal field. The EPR spectrum of the (AN) sample (Fig. 5) shows a featureless broad peak. The width of the line has narrowed upon annealing. The $C(=V^{4+}/V_{total})$ values for the (UN) and (AN) samples were calculated to be 0.0085 and 0.015, respectively. Furthermore, it was found that the spectra of (UN) and (AN) samples at 77 and 300 K were virtually identical. Sanchez *et al.* [10] reported $C = 0.01$ for V_2O_5 gels, determined by EPR studies. However, Chung and Machenzie [1] used an indirect method of magnetic susceptibility to determine *C* values of the glasses in the system 55 V_2O_5–45 GeO_2. They obtained *C* ranging from 0.10 to 0.26, depending on the glass preparation conditions.

4. Discussion

Khan *et al.* [3], while measuring the electrical conductivity of V_2O_5–GeO_2 glasses as a function of temperature noted a sudden rise in the conductivity at about 240° C. They related this effect to the microstructure formation. In the present investigations this was confirmed by electron microscopy and differential scanning calorimetry.

The general appearance of the absorption spectrum (Fig. 3) is similar to those observed from the other vanadium glasses, for example V_2O_5–P_2O_5 glasses [13, 14] and V_2O_5–P_2O_5–TeO_2 [14]. It is surprising to note that the glass former has apparently very little effect on the optical absorption of these glasses. However, Ioffe *et al.* [15] have suggested that the glass-forming oxide might be simply a non-interacting solvent in the electrical conduction process. Two general regions of absorption are of interest in

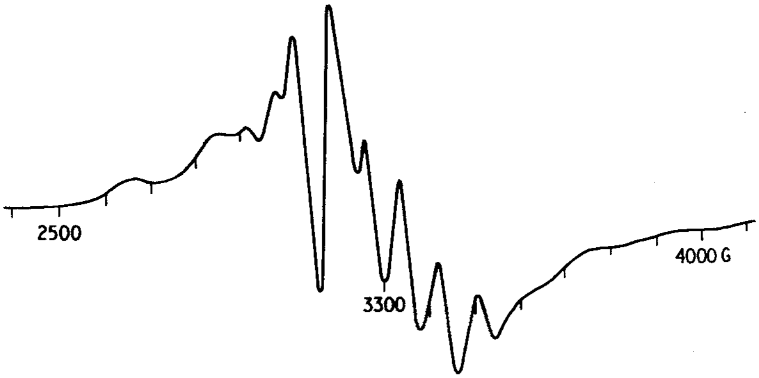

Figure 4 EPR spectrum at room temperature of the unannealed (UN) sample. (Spectrometer settings were as follows: signal average = 4 times; digitization = 2048 points; field set = 3306 G; scan range = 2000 G; scan time = 120 sec; modulation frequency = 100 kHz; modulation amplitude = 5G; gain = 2 × 10^2; time constant = 0.016 sec; microwave power = 15 dB and microwave frequency = 9.106 GHz).

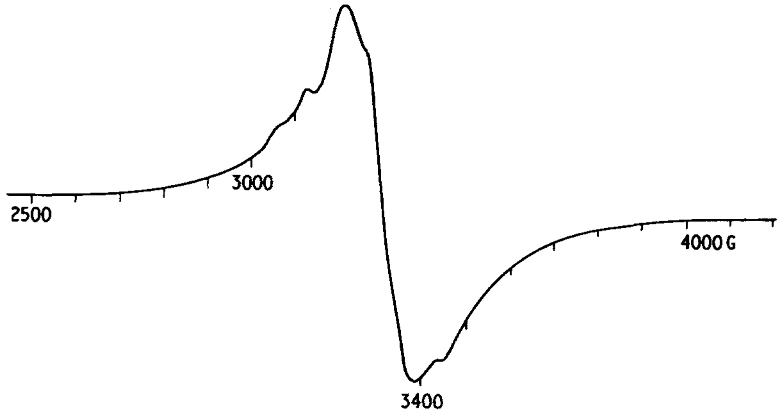

Figure 5 EPR spectrum at room temperature of the annealed (AN) sample. Spectrometer settings were the same as for the (UN) sample (Fig. 4) except that gain = 80.

the glasses. First, there is a broad absorption tail that extends to longer wavelength (say, from 550 to 900 nm), and second, the absorption edge near about 550 nm (Fig. 3). It is clear from the figure that absorption is increased upon annealing the sample. The possible effects responsible for this change may be (a) microstructure formation, (b) valency change in vanadium ions, or (c) a combination of both, which take place on annealing (section 3).

The reduced long wavelength tail is expected from the formation of the microstructure alone, because there exist sharp edges in the density of states in the conduction and the valence bands in crystalline semiconductors, whereas in amorphous semiconductors some states are extended in the forbidden gap. Furthermore, Anderson *et al.* [13] in their study of V_2O_5–P_2O_5 glasses reported that the tail for samples of comparable thickness is much stronger than that observed in crystalline V_2O_5. However, Fig. 3 shows results, contrary to these, suggesting that microstructure formation alone is not responsible for the change in optical spectrum.

Anderson *et al.* [13] have reported that V^{4+} ions in V_2O_5–P_2O_5 glasses may contribute significantly to this broad absorption tail (Fig. 3). The EPR measurements revealed that $C(=V^{4+}/V_{\text{total}})$ was about 0.0085 for the (UN) sample and 0.015 for the (AN) sample (i.e. an increase of about two fold). This cannot fully account for the observed change in the optical absorption which is about three to four fold (optical density is directly proportional to the concentration, Beer's law [16]).

Bamford [16] reported that vanadium in the soda–lime–silica glass system, can exist in three ionic species, namely V^{5+}, V^{4+} and V^{3+}. The absorption band at 530 nm was assigned by them to V^{5+}, the bands at 425 and 645 nm to V^{3+} and band at 1100 nm to V^{4+}. Since the glass former has very little effect on the optical absorption, we may therefore assume that the absorption tail (Fig. 3) arises from the combination of the bands associated with V^{3+} and V^{4+} ions in the glass. The absorption coefficients for V^{3+} and V^{4+} in this wavelength range are very similar in magnitude [17]. The optical data suggest that the combined concentrations of V^{3+} and V^{4+} ions in the (AN) sample is about three to four times that of the UN sample.

It may be mentioned that energy level separations of paramagnetic ions of the order of $10\,\text{cm}^{-1}$ ($8.25\,\text{cm}^{-1}$ for V^{3+} in α-Al_2O_3 [18]) in general cannot be readily observed with conventional paramagnetic resonance techniques. The most accurate values are those obtained for V^{3+} using far-infrared Fourier-transform spectroscopy [18]. Thus EPR technique is not suitable for measuring the concentration of V^{3+} ions. Below we offer plausible explanations for the increase in concentration of V^{3+} and V^{4+} ions upon annealing.

Vanadium pentoxide has a melting point of 668° C and germanium dioxide has a melting point of 1086° C. The ionic character of V–O and Ge–O bonds calculated using Pauling's electronegativity principle are 65% and 43% respectively. The pentoxide loses oxygen reversibly in the region 700 to 1125° C, a phenomenon which may account for its important catalytic properties [19].

Molten V_2O_5 at temperature just above the melting point dissociates [17, 20] according to

$$V_2O_5 \rightleftharpoons V_2O_{5-x} + (x/2)O_2 \qquad (1)$$

where x increases with increasing temperature. For every atom of oxygen evolved two electrons are left behind. Among many possibilities are (a) the electrons are singly trapped at separate V^{5+} centres yielding two V^{4+} centres and (b) the two electrons are trapped at one V^{5+} centre giving rise to one V^{3+} centre. The oxidation–reduction equilibria can be described in terms of the reactions

$$2O^{2-} + 4V^{5+} \rightleftharpoons 4V^{4+} + O_2 \qquad (2)$$

$$4O^{2-} + 4V^{5+} \rightleftharpoons 4V^{3+} + 2O_2 \qquad (3)$$

The equilibrium expression between V^{4+} and V^{3+} can simply be obtained by subtracting Equation 2 from Equation 3.

$$2O^{2-} + 4V^{4+} \rightleftharpoons 4V^{3+} + O_2 \qquad (4)$$

Of the three redox equilibria, only two are independent equilibrium expressions. The increase in the conductivity of the annealed sample could be due to the fact that upon annealing at 300° C for 24 h, significant quantities of all three vanadium valence states could easily coexist in view of the sufficiently close values of the equilibrium constants [17] for the equilibrium expressions above. If both V^{3+} and V^{4+} are produced in the annealed sample, the three-fold increase in the optical density of the annealed sample in the wavelength range of 400 to 800 nm is due to the increase of V^{3+} and V^{4+} ions in the annealed sample, while the EPR data detects only the increase of V^{4+} ions. Crystals made when large quantities of V_2O_5 is added to the MgO melt [21, 22] were observed to be almost black because of large concentrations of V^{3+}. The change in colour of the sample from yellowish-green before annealing to brown after annealing could also be due to a change in the oxidation state of the vanadium from V^{3+} to V^{4+}. This was suggested as the reason for the colour change on heating of blue zoisite [23]. Conventional methods for qualitative analysis [23] are often destructive and relatively time-consuming. EPR may be employed more efficiently to characterize the materials containing such ions.

The EPR spectrum of the annealed sample (Fig. 5) shows that the width of the line has narrowed after annealing the sample at 300° C. This can be attributed to the process of exchange narrowing [24]. As the concentration of the V^{4+} increases during microstructure formation, the hyperfine lines coalesce to a single line. This exchange interaction has also been observed in the EPR investigation of the variation of paramagnetic V^{4+} ions in polycrystalline WO_3-doped V_2O_5 [12] and in semiconductive glasses of the V_2O_5–P_2O_5 system [25–27]. We found that the spectra of the annealed and the unannealed samples at 77 and 300 K were virtually identical indicating that this exchange mechanism was independent of temperature. The temperature invariance of the EPR spectrum also indicates that the hopping frequency is smaller than the linewidth [12].

5. Conclusion

The increase in the optical density and the spin concentration of the annealed sample of V_2O_5–GeO_2 (1:1 M %) over the unannealed sample can be explained by a reduction of the V^{5+} oxidation state of vanadium pentoxide to +4 and +3. The EPR technique gives an indication of the presence of the +4 valence state since the $3d^1$ configuration is paramagnetic and yields an EPR spectrum typical for a 3d electron localized on a single ^{51}V nucleus. Thus the two-fold increase in the spin concentration of the annealed sample can be attributed to an increase in the V^{4+} concentration. The data from optical absorption spectroscopy showed a three-fold increase in the optical density of the annealed sample which could be explained by an increase in the concentration of V^{3+} and V^{4+} ions. The data from EPR and optical absorption spectroscopy are consistent with the assumption that while annealing in the open air for 24 h at 300° C, V_2O_5 undergoes reduction to V^{4+} and V^{3+} via an oxidation–reduction process in which V_2O_5 dissociates according to Equation 1.

It would be interesting to repeat the same experiment and anneal the sample in an inert atmosphere like nitrogen or argon to learn more about the effect of oxygen partial pressure on the oxidation–reduction equilibria of vanadium pentoxide, since one would expect that more V^{4+} and V^{3+} ions would be produced as predicted by the La Chatelier principle. However, it should be noted that the relevant oxygen pressure is not that in the atmosphere above the melt but is that effective in the glass environment of the multivalent vanadium ion.

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