

Relaxation studies on V_2O_5 - TeO_2 glasses using heterogeneous conductor model

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Abstract. The dielectric modulus spectra of glasses in the system V_2O_5 - TeO_2 have been studied as a function of frequency in the temperature range 230 to 330 K. A heterogeneous conductor model developed recently with the assumption of a sinusoidally varying local conductivity in the conducting phase has been successfully applied to analyse the data in this glass system. The Kohlrausch-Williams-Watts (KWW) stretched exponential function has also been used to fit the measured modulus spectra. The exponent β is found to be correlated to the conductivity fluctuation in the conducting phase as assumed in the heterogeneous model.

Keywords. Relaxation studies; V_2O_5 - TeO_2 ; heterogeneous conductor model.

1. Introduction

Conductivity relaxation study in oxide glasses has been an active area of research in recent years (Elliott and Owens 1989; Ngai *et al* 1989; Funke 1991). The relaxation results have in the most cases been analysed using the stretched Kohlrausch-Williams-Watts (KWW) exponential function (Elliott and Owens 1989). Such a non-Debye relaxation behaviour has been explained on the basis of a many-body interaction involving the jumping ion and the other ionic species within the glass structure (Funke 1991). The dielectric relaxation spectra of certain oxide glasses have recently been analysed on the basis of a diagonal layer model (Yamamoto and Namikawa 1989). A modified version of this model has been used by us to calculate the electrical modulus spectra of alkali-containing silicate glasses as well as some phosphate glasses containing transition metal ions (Saha and Chakravorty 1992a). Though the model has been found to be valid for silicate glasses containing different alkali species (Saha and Chakravorty 1992b), we have not so far tested the applicability or otherwise of the same to transition metal ion-containing glasses with different glass-formers. We have investigated the relaxation spectra of glasses in the V_2O_5 - TeO_2 system in relation to our diagonal layer model. The latter is found to give results in satisfactory agreement with the experimental data. The details are reported in this paper.

2. Model

We have described the heterogeneous conductor model in detail elsewhere (Saha and Chakravorty 1992a). Here we summarize the basic features of the model and the equations used for the analysis of ac conductivity data. The glass sample is described in terms of two phases—one conducting and the other insulating. The configuration of these two layers as assumed in our model is shown in figure 1. Most of the

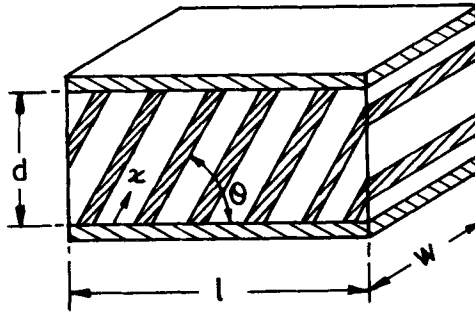


Figure 1. Schematic of heterogeneous conductor model.

alkali-containing glasses we have studied so far do exhibit a two-phase co-continuous structure. The glass system investigated in this work also shows a phase-separated structure.

In our model we assume a fluctuation in the transition metal ion concentration in the conducting phase which is represented by a local conductivity variation as shown below:

$$\sigma_x = \sigma_0 + \sigma \sin \frac{2\pi x}{\lambda}, \quad (1)$$

where σ_x is the conductivity at a distance x from the electrode along the conducting path, σ_0 a constant, σ the amplitude, and λ the wavelength of conductivity variation. The impedance Z of the sample with length l , thickness d and width w can be shown to be given by (Saha and Chakravorty 1992a)

$$\frac{l}{Z} = \frac{nWl}{d} \frac{l}{\left[\sum_{i=1}^n \frac{1}{y'_i + jy''_i} \right]}, \quad (2)$$

where

$$y'_i = \frac{\epsilon_\infty \alpha \omega^2 \tau_{ix} \cos^2 \theta}{(1 - \alpha)(1 + \omega^2 \tau_{ix}^2)} + \frac{\epsilon_\infty \alpha \sin^2 \theta}{\tau_{ix}(1 - \alpha)}, \quad (3)$$

$$y''_i = \omega \epsilon_\infty \left[1 + \frac{\alpha \cos^2 \theta}{(1 - \alpha)(1 + \omega^2 \tau_{ix}^2)} \right], \quad (4)$$

$$\tau_{ix} = \frac{\epsilon_\infty}{\left(\sigma_0 + \sigma \sin \frac{2\pi x}{\lambda} \right) (1 - \alpha)}, \quad (5)$$

where ϵ_∞ is the high-frequency dielectric constant (assumed to have identical values in both the phases of this model), α the volume fraction of the conducting phase and n the total number of slices into which each sinusoid of the conductivity variation within the conducting layer has been divided. A value of $n = 1000$ has been used in our calculations. It should be noted that λ does not ultimately appear in any of the equations written above, because the summation of contributions from narrow strips of thickness δ_x is computed and the total number of such strips is taken as n .

The dielectric modulus M^* defined as (Macedo *et al* 1972)

$$M^* = M' + jM'' = \frac{1}{\epsilon^*}, \quad (6)$$

ϵ^* being the complex dielectric permittivity, has been shown to be given by the following equations (Saha and Chakravorty 1992a):

$$M' = \frac{\omega\epsilon_0}{n} \left[\sum_{i=1}^n \frac{y_i''}{y_i'^2 + y_i''^2} \right], \quad (7)$$

and

$$M'' = \frac{\omega\epsilon_0}{n} \left[\sum_{i=1}^n \frac{y_i'}{y_i'^2 + y_i''^2} \right], \quad (8)$$

where ϵ_0 is the free space permittivity.

The expression for dc resistivity ρ is

$$\rho = \frac{1}{n} \sum_{i=1}^n \frac{\tau_{ix}(1-\alpha)}{\epsilon_\infty \alpha \sin^2 \theta}. \quad (9)$$

The experimental values of M' and M'' are least-square fitted to (7) and (8) using σ , σ_0 , α and θ as parameters.

In the model delineated above, a fixed value of θ has been assumed for the inclination of the conducting layer with respect to the electrodes. A more realistic assumption would be a distribution of θ values. This was tried by considering a Gaussian distribution of θ around a mean value. The results, however, remain unaltered with respect to those obtained by assuming a fixed value of θ . This implies that the layers having an angular orientation around 45° with respect to the two electrodes contribute the most to the observed relaxation spectrum.

3. Experimental

Table 1 summarizes compositions of the different glasses investigated. Glasses were prepared by melting a suitable mixture of the analytical reagent grade oxides in alumina crucibles in an electrically heated furnace at a temperature around 1173 K. Glasses were cast by pouring the melts onto a brass plate.

For electrical measurement samples with a typical area of 1 cm^2 and thickness $\sim 0.08 \text{ cm}$ were polished with different mesh sizes of silicon carbide grit and finally in $0.5\text{-}\mu\text{m}$ -size alumina powder. The two opposite faces of the samples were coated with silver paint electrodes (Electrodag 1415) supplied by Acheson Colloiden B.V., Holland. The specimen was mounted in a holder and the electrical impedance measured with a Hewlett-Packard 4192A impedance analyzer in the frequency range 100 Hz to 1 MHz. Measurements were carried out over the temperature range 230 to 330 K with the temperature control being accurate to within $\pm 1 \text{ K}$. The bulk electrical resistivity was determined by the complex impedance analysis of the frequency-dependent capacitance and resistance data (Chakravorty and Shrivastava 1986).

Table 1. Composition (in mole%) for different glasses.

Glass No.	V ₂ O ₅	TeO ₂
1	70	30
2	80	20
3	90	10

4. Dielectric modulus analysis

The electrical modulus data were also analysed on the basis of the (KWW) stretched exponential function given by (Ngai *et al* 1984a)

$$F(t) = \exp[-(t/\tau_R)^\beta], \quad (10)$$

where τ_R denotes the conductivity relaxation time and the exponent β has a value between 0 and 1. We write the decay function as (Moynihan *et al* 1973)

$$F(t) = \sum_{i=1}^m g_i \exp(-t/\tau_i), \quad (11)$$

where the g_i 's are the coefficients of the exponential terms used to expand the function $F(t)$, m the total number of such terms taken here to be equal to 14, and the τ_i 's multiples of τ_R which are selected to cover the range of (t/τ_R) in which $F(t)$ has an appreciable time dependence.

The real and imaginary parts of the dielectric modulus $M^*(\omega)$ in the frequency domain can be written as (Saha and Chakravorty 1992b)

$$M'(\omega) = M_s \left[1 - \sum_{i=1}^m \frac{g_i}{1 + \omega^2 \gamma_i^2 \tau_R^2} \right], \quad (12)$$

and

$$M''(\omega) = M_s \sum_{i=1}^m \frac{g_i \gamma_i \omega \tau_R}{1 + \omega^2 \gamma_i^2 \tau_R^2}, \quad (13)$$

where

$$\gamma_i = \tau_i/\tau_R \text{ and } M_s = 1/\epsilon_\infty. \quad (14)$$

The values of g_i and γ_i were obtained by a least-square fitting of the experimental $M'(\omega)$ and $M''(\omega)$ values with the expressions given by (12) and (13) respectively. The β value was evaluated by a least-square fitting of the right hand sides of (10) and (11) respectively using the g_i and γ_i values determined from the previous step. We have reported on the detailed procedure elsewhere (Saha and Chakravorty 1990).

5. Results and discussion

Figure 2 is an electron micrograph for glass no. 1. An interconnected phase structure is evident. This is typical of the microstructure in other glasses. It appears therefore that one of the phases is rich in vanadium ions and it corresponds to the conducting phase as postulated in our heterogeneous conductor model. In figure 3 are shown the

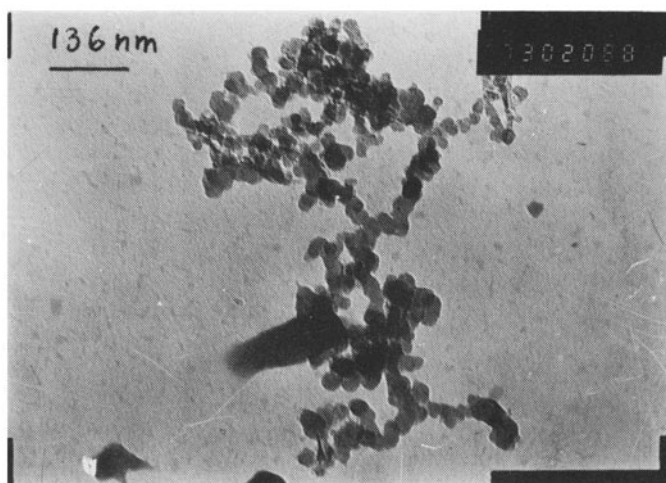


Figure 2. Transmission electron micrograph for glass no. 1

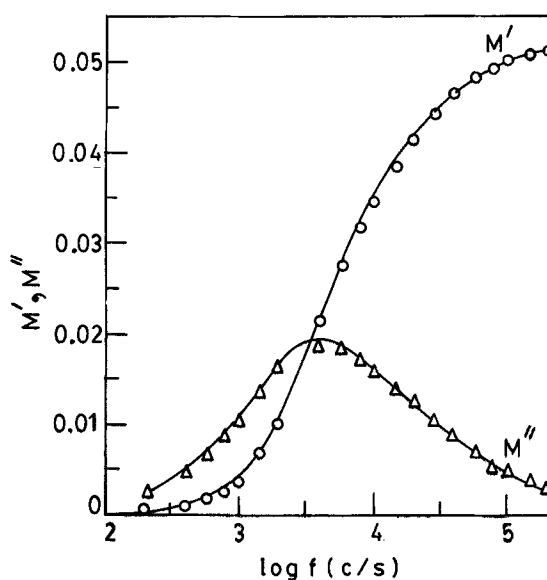


Figure 3. Variation of M' and M'' as a function of frequency for glass no. 1 at 268 K (analysis by KWW model); (—) theoretical curve.

variation of M' and M'' respectively as a function of frequency for glass no. 1 at a temperature of 268 K. The points in this figure represent the experimental data and the solid lines are the theoretical curves as obtained by the β -analysis delineated in the previous section. Satisfactory agreement between the experimental results and theoretical values is evident. This is typical for all the glasses and different temperatures. The β values estimated for the different glasses are summarized in table 2. It can be seen that the β value does not change with temperature in the case of

Table 2. Values of β and ϵ_∞ for various glasses at different temperatures.

Glass No.	Temperature (K)	ϵ_∞	β
1	268	19.4	0.74
	280	—	—
	297	—	—
	313	—	—
	326	—	—
2	263	18.9	0.73
	273	—	—
	284	—	—
	295	—	—
	310	—	—
3	228	20.3	0.76
	263	—	—
	275	—	—
	284	—	—
	292	—	—

all the glasses in the present series. It could be due to the fact that the measurements have been carried out far below the glass transition point. Also, the range of temperature used is narrow. The latter effect has been reported by other investigators also (Ngai *et al* 1984b). The value of the high-frequency dielectric constant ϵ_∞ decreases a little as the V_2O_5 concentration is increased from 70 to 80 mol% and then increases again as the concentration is brought to a value of 90 mol%. The high dielectric constant for the present glasses is evidently a property of the TeO_2 glass-former and the change in dielectric constant has been correlated to the change in bond energies of Te–O and V–O respectively when the bond length increases (Mansingh and Dhawan 1983). The β value in the present series of glasses shows an increasing trend as the ϵ_∞ value increases.

Figures 4a and 4b show the variation of M' and M'' respectively as a function of frequency at different temperatures for glass no. 1 as calculated by the heterogeneous conductor model. The points in these figures represent the experimental data and the solid lines the theoretical curves. Satisfactory agreement between the two is evident over most of the frequency range. A small discrepancy, however, is discernible at higher frequencies. These results are typical of all the glasses studied. The values of the least-square fitted parameters for different glasses are summarized in table 3. It should be mentioned here that the values of α and θ estimated for any temperature have been kept fixed for subsequent minimization at other temperatures. The rationale is that the glass structure at the micro-level is unlikely to change below the glass transition temperature where the measurements are carried out. In figure 5 are shown the experimentally and theoretically calculated dc resistivity values for different glasses as a function of temperature. The points represent the experimental data and the line has been drawn through the theoretically calculated resistivity values. Satisfactory agreement between the two sets of results is evident. In table 4 the theoretical and experimental activation energy values ϕ_{dc} for the three glasses are compared.

From tables 2 and 3 we find that the β value could be correlated to the

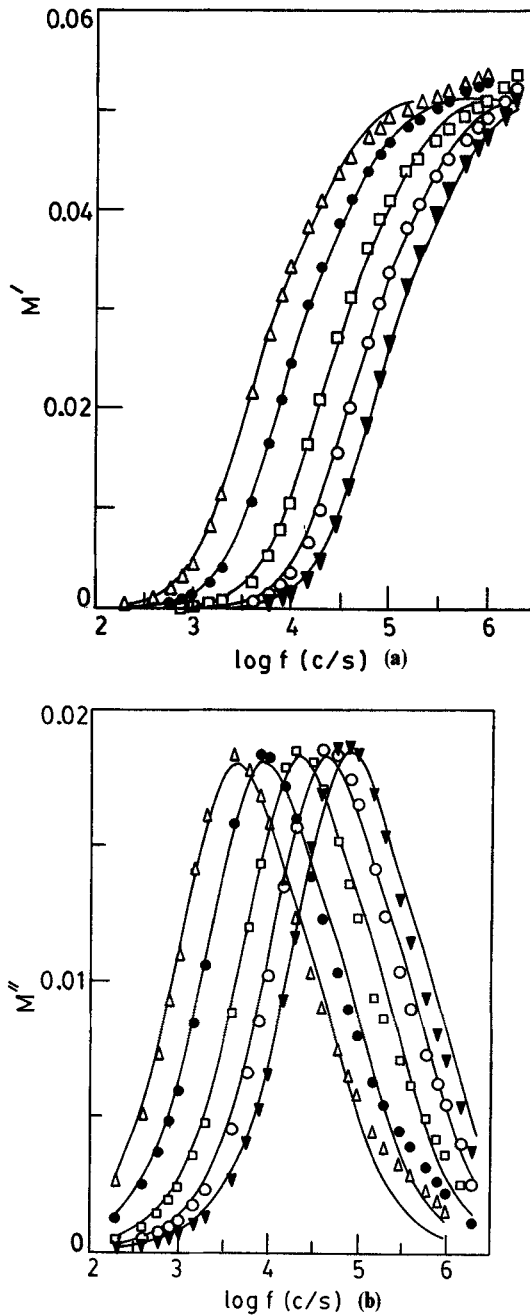


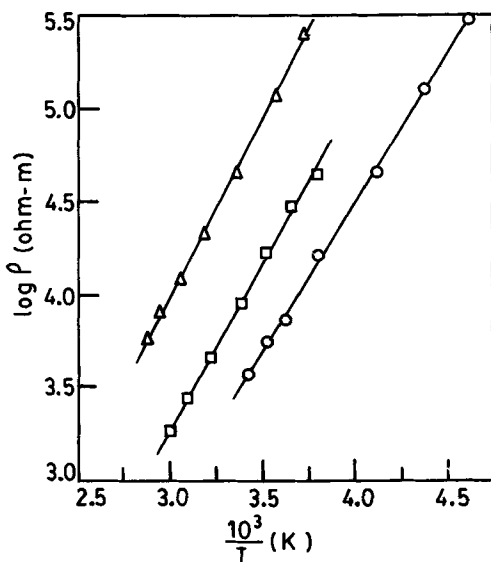
Figure 4. a. Variation of M' as a function of frequency for glass no. 1 (analysis by heterogeneous conductor model); (—) theoretical curve; (Δ) 268 K, (\bullet) 280 K; (\square) 297 K, (\circ) 313 K, (\blacktriangledown) 326 K. b. Variation of M'' as a function of frequency for glass no. 1 (analysis by heterogeneous conductor model); (—) theoretical curve; (Δ) 268 K, (\bullet) 280 K, (\square) 297 K, (\circ) 313 K, (\blacktriangledown) 326 K.

Table 3. Parameters in the heterogeneous conductor model for various glasses.

Glass No.	Temperature (K)	σ_0 ($10^{-5}\text{ohm}^{-1}\text{m}^{-1}$)	σ ($10^{-5}\text{ohm}^{-1}\text{m}^{-1}$)	α	θ	$\sigma_{\text{max}}/\sigma_{\text{min}}$
1	268	1.6	1.0	0.4	41°	4.8
	280	3.3	2.2	—	—	4.8
	297	8.4	5.5	—	—	4.8
	313	16.9	11.0	—	—	4.8
	326	30.0	19.7	—	—	4.8
2	263	7.8	5.2	0.4	41°	5.0
	273	14.5	9.7	—	—	5.0
	284	25.0	16.7	—	—	5.0
	295	43.0	28.8	—	—	5.0
	310	81.0	54.0	—	—	5.0
3	228	2.8	1.8	0.4	40°	4.6
	263	22.0	14.0	—	—	4.5
	275	45.0	28.8	—	—	4.5
	284	67.0	43.0	—	—	4.6
	292	100.0	63.0	—	—	4.4

Table 4. Experimental and theoretical values of dc activation energies for different glasses.

Glass No.	$\phi_{\text{dc}}(\text{eV})$	
	Exp.	Theor.
1	0.38	0.38
2	0.35	0.35
3	0.31	0.31

**Figure 5.** Variation of dc resistivity as a function of temperature for different glasses. Experimental: (Δ) glass no. 1, (\square) glass no. 2, (\circ) glass no. 3 and theoretical (—).

fluctuation in conductivity of the vanadium-rich layer used in the present model. The ratios of the maximum and minimum conductivity in the conducting layer as estimated from the parameters σ_0 and σ for the different glasses are shown in the last column of table 3. It is seen that the ratio $\sigma_{\max}/\sigma_{\min}$ does not change much as a function of temperature for the different glasses. Moreover, it is evident that this value increases as the β value is reduced. It is therefore concluded that a smaller value is associated with a larger fluctuation of vanadium ion and *vice versa*. It should also be noted that the parameters σ and σ_0 show an exponential temperature dependence with an activation energy identical to ϕ_{dc} . This shows that the spatial variation of conductivity σ_x arises due to fluctuation of vanadium ion concentration within the conducting phase of our model.

Comparing the ratios of $\sigma_{\max}/\sigma_{\min}$ as obtained in the present series with those computed in the case of lithium silicate glasses (Saha and Chakravorty 1992a), it is noted that the ratio for the V_2O_5 - TeO_2 samples is around 4.5 whereas for the silicate glasses it varies from 7 to 10 for Li_2O concentration up to 20 mole%. For the latter with 30 mole% Li_2O , however, the value is around 5.0. The physical implication is that the fluctuation of vanadium ions within the conducting phase is less than that of lithium ions in silicate glasses. The reason for such a difference can be sought in the viscosity of the respective glass melts before they are quenched at room temperature. Evidently, V_2O_5 - TeO_2 glasses are more fluid than silicate glasses at the temperature from which they are ultimately quenched. In other words, the diffusion kinetics of vanadium ions in the former is faster than that of lithium ions in the latter. Another interesting feature of the present results is the fact that the $\sigma_{\max}/\sigma_{\min}$ ratio for V_2O_5 - TeO_2 is smaller than that in V_2O_5 - P_2O_5 glasses (Saha and Chakravorty 1992a). Also, in the latter $\sigma_{\max}/\sigma_{\min}$ decreases as the P_2O_5 content is increased. In V_2O_5 - TeO_2 series, on the other hand, the corresponding value does not show significant change as the TeO_2 content is increased. Physically this implies that the fluidity of V_2O_5 - TeO_2 melt is relatively insensitive to the TeO_2 concentration.

In summary, the heterogeneous conductor model has been successfully applied to V_2O_5 - TeO_2 glass system. The theoretically calculated modulus spectra are in satisfactory agreement with the experimental results. The KWW exponent β is related to the vanadium ion fluctuation within the conducting phase—a higher fluctuation leading to a smaller value of β . The dc resistivity variation of the glasses as a function of temperature can be reproduced satisfactorily from the theoretical model.

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