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ENTHALPIC RELAXATION OF $25Na_2O{\cdot}xTiO_2{\cdot}(75\text{-}x)SiO_2$ GLASSES

M. Liška[1*], *J. Antalík*[2] *and I. Štubna*[3]

[1]Institute of Inorganic Chemistry, Slovak Academy of Sciences, M. Rázusa 10
911 01 Trenčín
[2]Faculty of Chemical Technology, Slovak Technical University, Radlinského 9
812 37 Bratislava
[3]College of Education, A. Hlinku 1, 949 74 Nitra, Slovakia

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Abstract

The enthalpic relaxation of the title glasses, studied by differential scanning calorimetry, is well described by a mathematical model based on the stretched exponential relaxation function with the relaxation time proportional to the actual viscosity. The dependence of viscosity on temperature and the fictive temperature was expressed by Mazurin's approximation. The relaxation parameters obtained correlated significantly with the glass composition, indicating the changes in the structural of the TiO_2 role near a TiO_2 content of 3–4 mol%.

Keywords: DSC, glass, relaxation, structure

Introduction

Various physical properties of titania-bearing silicate melts and glasses are well known to display unusual behaviour [1–3]. These phenomena may be rationalized in terms of the structural role of TiO_2, which depends on the chemical composition and temperature, i.e. on its network-forming/modifying character and the changeable oxygen coordination number of Ti^{4+}. The observed temperature and compositional control of various properties may be explained on the basis of homogeneous equilibria between the different coordination states of Ti, in which the other system components, i.e. alkalis and SiO_2, take part [1, 2].

X-ray emission spectroscopy has revealed both octahedral and tetrahedral coordination of Ti in partially depolymerized sodium titanium silicate glasses [4]. An X-ray absorption study of Ti-bearing silicate glasses yielded qualitatively similar results [5]. These results are in accordance with the large positive excess volumes reported by Dingwell [6] for the Na_2SiO_3–TiO_2 system.

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[*] Author for correspondence: e-mail: liska@uach1.savba.sk

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The existence and distribution of various structural motifs in silicate melts and glasses are typically examined by Raman spectroscopy. Unfortunately, unambiguous assignment of the Raman bands associated with Ti^{4+} is not possible at the present time [2]. On the other hand, the interpretation of the results obtained by Henderson and Fleet [3] by micro-Raman spectroscopy is quite different. The Raman spectra of Na_2SiO_3–TiO_2 glasses exhibit no indication of hexacoordinated Ti. Ti is tetracoordinated at low TiO_2 content, but predominantly pentacoordinated at TiO_2 contents greater than 10 mol%. Markgraf and Sharma [7] proposed Ti penta-coordination in fresnoite glass on the basis of Raman spectroscopy.

Some indirect structural information may be extracted from the compositional trends in various physical properties, including the viscosity, viscous flow activation energy, heat capacity, molar volume, molar refractivity and thermal expansion coefficient. The changes in the structural role of some glass constituent at a particular glass temperature and chemical composition are expected to be expressed by significant points (e.g. local extremes or discontinuities in slope) in the property – temperature – composition dependences.

The present paper deals with the enthalpic relaxation of the title glasses. The compositional dependence of the molar heat capacities and parameters of the relaxation model are studied with reference to the changes in the structural role of TiO_2.

Method

The Tool [8] and Narayanaswamy [9] model of structural relaxation describes the DSC curves near the glass transition temperature [10]. The molar enthalpy $H(T, T_{f,H})$ of a sample characterized by thermodynamic temperature T and fictive (structural) temperature $T_{f,H}$ is given by

$$H(T,T_{f,H}) = H(T_r,T_r) + \int_{T_{f,H}}^{T} C_{pg}(T')\mathrm{d}T' + \int_{T_r}^{T_{f,H}} C_{pm}(T')\mathrm{d}T' \qquad (1)$$

where C_{pg} and C_{pm} are the isobaric molar heat capacities of the glass and metastable glass-melt, respectively. T_r is an arbitrary, but sufficiently high reference temperature. The time course of the effective molar heat capacity $C_{p,eff}(t)$ measured during the DSC experiment may be obtained from the definition

$$C_{p,eff}(t) = C_{pg}[T(t)] + \{C_{pm}[T_{f,H}(t)] - C_{pg}[T_{f,H}(t)]\}\frac{\mathrm{d}T_{f,H}}{\mathrm{d}T} \qquad (2)$$

On the assumption of the temperature independence of C_{pm} and the linear temperature dependence of the glass heat capacity

$$C_{pg}(T) = C_{pg,0} + C_{pg,1}T \tag{3}$$

Eq. (2) reduces to

$$C_{p,eff}(t)=C_{pg,0}+C_{pg,1}T(t)+\{C_{pm}-C_{pg,0}-C_{pg,1}T_{f,H}(t)\}\frac{dT_{f,H}}{dT} \tag{4}$$

For a given time–temperature schedule $T(t)$, the time dependence of fictive temperature $T_{f,H}(t)$ is obtained from the integral equation

$$T_{f,H}(t) = T(t) - \int_0^t dt'\left(\frac{dT}{dt}\right)_{t'} M_H[\xi(t) - \xi(t')] \tag{5}$$

where M_H is the relaxation function of dimensionless time ξ, which is defined as a time – integral of inverse relaxation time τ_H:

$$\xi(t) = \int_0^t \frac{dt'}{\tau_H(t')} = \int_0^t \frac{K_H}{\eta(t')}dt' \tag{6}$$

On the right-hand side of Eq. (3), the relaxation time is expressed as proportional to the dynamic viscosity η [9, 11, 17]:

$$\tau_H = \eta(T, T_{f,H})/K_H \tag{7}$$

where the subscript H (enthalpy) reflects the dependence of the material parameter K on the particular property studied.

The relaxation function may be expressed by the stretched exponential function (also known as the Kohlrausch-Williams-Watts function - KWW) [12]:

$$M_H(\xi) = \exp(-\xi^b) \tag{8}$$

where the exponent b has a value between 0 and 1.

Through use of the above relaxation function, the following relationship was found for the temperature derivative of the fictive temperature:

$$\frac{dT_{f,H}}{dT} = \left(\frac{dT}{dt}\right)_t \frac{bK_H}{\eta[T(t),T_{f,H}(t)]} \int_0^t dt'\left(\frac{dT}{dt}\right)_{t'} [\xi(t) - \xi(t')]^{b-1} M_H[\xi(t) - \xi(t')] \tag{9}$$

which allows calculation of the theoretical DSC curve according to Eq. (4).

The final question is the dependence of the viscosity on both the fictive and thermodynamic temperatures $\eta=\eta(T,T_{f,H})$. At metastable equilibrium where $T_{f,H}=T$, the temperature dependence of the viscosity of glass-forming liquids is represented by the empirical Vogel-Fulcher-Tamman (VFT) equation:

$$\log[\eta(T,T_{\mathrm{f,H}}=T)] = A + B/(T - T_0) \tag{10}$$

where A, B and T_0 are empirical constants and composed brackets denote the numerical value of viscosity. The simple Arrhenius-like equation

$$\log[\eta(T,T_{\mathrm{f,H}}=\mathrm{const.})] = A'(T_{\mathrm{f,H}}) + B'(T_{\mathrm{f,H}})/T \tag{11}$$

can be used for the non-equilibrium glassy state where $T_{\mathrm{f,H}}$ is constant. Mazurin [10, 13, 14] proposed a simplified model of this dependence, assuming that all the isostructural viscosity lines have one common point with the coordinates $\{1/T=0, \log\eta=\log\eta_0\}$ in the $\log\eta$ *vs.* $1/T$ plot. When Eqs (6) and (7) are combined with Mazurin's approximation, the following formula for non-equilibrium viscosity is obtained:

$$\log[\eta(T,T_{\mathrm{f,H}})] = \log[\eta(T_{\mathrm{f,H}},T_{\mathrm{f,H}})]\frac{T_{\mathrm{f,H}}}{T} - \log[\eta_0]\left(\frac{T_{\mathrm{f,H}}}{T} - 1\right) \tag{12}$$

The time course of the effective molar heat capacity $C_{\mathrm{p,eff}}(t)$ (e.g. the DSC measurement output) may now be calculated from Eqs (1)–(12) for an arbitrary time – temperature schedule $T(t)$.

If it is presumed that the parameters A, B, and T_0 of the VFT viscosity equation are known, then the unknown parameters of the proposed regression model may be estimated by using the standard non-linear least squares method, i.e. minimizing the target function

$$F(C_{\mathrm{pg,0}},C_{\mathrm{pg,1}},C_{\mathrm{pm}},K_{\mathrm{H}},\eta_0,b) = \int_0^{t_{\max}} \left[C_{\mathrm{p,eff}}^{\mathrm{clc}}(t) - C_{\mathrm{p,eff}}^{\mathrm{exp}}(t)\right]^2 \mathrm{d}t \tag{13}$$

where $t_{\max}$ is the time of completion of the DSC experiment.

Experimental

Batches were prepared by mixing powdered components of analytical grade purity: TiO_2 (anatase, Aldrich, 99.9+%), Na_2CO_3 (Lachema, pro analysis) and quartz glass (Optical Institute, St. Petersburg). These batches were melted in a furnace at temperatures between 1500 and 1530°C in a Pt–10%Rh crucible. Homogeneity was ensured by hand mixing. Each melt was poured from the crucible onto a stainless steel plate. The samples were tempered in a muffle furnace for 1 h at 600°C, the furnace was then switched off and the samples remained there until room temperature was reached. The chemical compositions of individual samples were determined by colorimetry (TiO_2 with tiron, i.e. 4,5-dihydroxy-1,3-benzenedisulfonic acid) and emission spectral analysis (Na_2O) after the samples had been decomposed with HF and H_2SO_4. The chemical compositions obtained, together with the sample numbering convention, are listed in Table 1.

Table 1 Chemical compositions of the glass samples investigated (mol%), and A, B, T_0 of the Vogel-Fulcher-Tammann (Eq. (2)), [15]. Standard deviations are presented in round brackets (e.g. 486.4(28) is equivalent to 486.4±2.8)

Glass	Na_2O	TiO_2	SiO_2*	A	B/K	T_0/K
PS1	24.08	0.00	75.92	–1.24(4)	3717(45)	486.4(28)
PS2	22.64	1.03	76.33	–1.61(3)	4145(36)	470.4(22)
PS3	21.28	2.46	76.26	–1.46(5)	3803(57)	515.2(36)
PS4	19.23	5.00	75.77	–1.80(4)	4176(38)	522.4(22)
PS6	17.32	7.85	74.38	–2.19(4)	4444(49)	538.6(27)

* Obtained as $100–Na_2O–TiO_2$

The DSC curves were measured with a Perkin Elmer PE5 differential scanning calorimeter. The compact cylindrical glass samples were first equilibrated at 600°C, and then cooled to room temperature at a cooling rate of 20°C min^{-1}. The DSC curves were recorded at a heating rate of 5°C min^{-1}.

The glass transition temperature T_{g-} was determined from the dilatometric cooling curve recorded on a TMA 402 thermomechanical analyser (Netzsch) at a cooling rate of 5°C min^{-1}.

Results and discussion

The coefficients of the VFT viscosity equation (Eq. (10)) for the studied glasses (Table 1) were taken from previous work [15].

About 50 experimental $C_{p,eff}^{exp}$ (T) points were considered in the regression analysis (Eq. (13)) for all the studied glasses. Two independent measurements (on two distinct glass samples) were considered for each glass composition. The

Table 2 The parameters of structural relaxation and their standard deviations in parentheses (e.g. 0.610(12) is equivalent to 0.610±0.012), the minima of the fictive temperature $T_{f,H}$(min) obtained during the cooling regime and the standard deviations of approximation s_{appr}

Glass	$\log(K_H/dPa)$	b	$T_{f,H}(min)/K$	$s_{appr}/J\ mol\ K^{-1}$
PS1	10.65(1) 10.62(1)	0.657(5) 0.667(5)	743 744	0.14 0.21
PS2	10.74(1) 10.68(1)	0.634(2) 0.645(6)	748 749	0.10 0.28
PS3	10.95(1) 10.84(1)	0.594(5) 0.608(5)	767 769	0.20 0.22
PS4	10.75(2) 10.85(1)	0.610(12) 0.611(5)	796 795	0.34 0.20
PS6	10.54(1) 10.53(1)	0.639(11) 0.647(10)	827 827	0.40 0.58

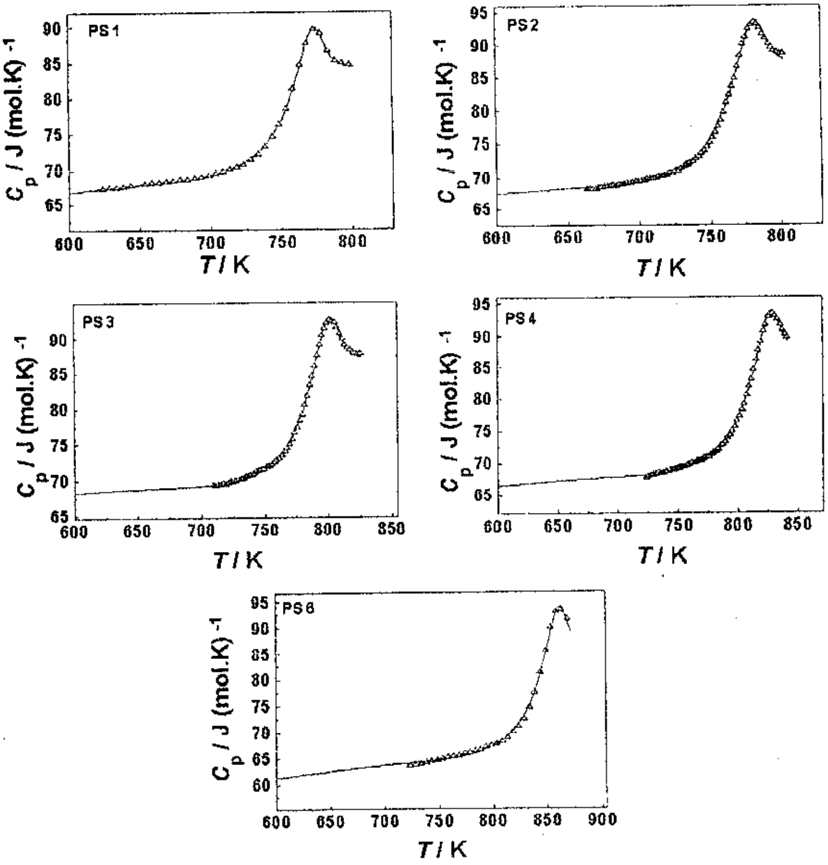

Fig. 1 Comparison of experimental (points) and calculated (solid line) DSC curves

details of the regression calculation algorithm used are given elsewhere [16]. The values of the standard deviation of approximation s_{appr} presented in Table 2 confirm the sufficient accuracy of the fits obtained for all the DSC curves. A comparison of the calculated and the experimental $C_{p,eff}(t)$ values is given in Fig. 1 (only one DSC curve is displayed for each glass composition). It can be seen that the model describes the experimental data with sufficient accuracy.

The estimates of the relaxation parameters, together with their standard deviations, are presented in Table 2. The values obtained are comparable with the results obtained for other silicate glasses [10].

The value of $\log(\eta_o/\mathrm{dP_{a.s}})=-1.14$ obtained previously [15] on the basis of the Adam and Gibs viscosity equation was used for all the DSC curves. Only the other two relaxation parameters (i.e. K_H and b) were determined in the regression analysis.

Table 3 The best estimates of molar heat capacities* with their standard deviations (e.g. 26.9(12) is equivalent to 26.9±1.2), and the corresponding correlation coefficients ρ

Glass	$C_{pg,0}$/ J (mol K)$^{-1}$	$10^3C_{pg,1}$/ J (mol K^2)$^{-1}$	C_{pm}/ J (mol K)$^{-1}$	ρ(g0,g1)	ρ(g0,m)	ρ(g1,m)
PS1	50.6(8)	26.9(12)	84.2(1)	–0.999	0.199	–0.205
	54.1(9)	29.9(14)	89.1(1)	–0.999	0.207	–0.213
PS2	65.3(7)	–8.2(11)	75.8(1)	–1.000	0.240	–0.246
	54.7(20)	21.3(28)	87.2(1)	–1.000	0.249	–0.255
PS3	62.8(27)	10.3(37)	87.6(1)	–1.000	0.204	–0.211
	60.9(28)	12.2(38)	87.1(1)	–1.000	0.205	–0.211
PS4	73.6(51)	–6.1(69)	87.3(2)	–1.000	0.348	–0.355
	56.4(20)	16.8(28)	87.4(1)	–1.000	0.322	–0.329
PS6	45.4(33)	26.4(44)	86.1(2)	–1.000	0.309	–0.317
	51.8(31)	20.0(40)	88.0(2)	–1.000	0.318	–0.326

* $C_{pg}(T)=C_{pg,0}+C_{pg,1}T$

$s^2(C_{pg})=s^2(C_{pg,0})+T^2s^2(C_{pg,1})+2Ts(C_{pg,0})s(C_{pg,1})\rho(g_0,g_1)$

The second subset of estimated parameters of the mathematical model (Eq. (13)) comprises the coefficients $C_{pg,0}$ and $C_{pg,1}$ of the linear temperature dependence of the molar heat capacity of glass $C_{pg}(T)$ and the temperature-independent molar heat capacity of the equilibrium glass melt C_{pm}. The results obtained are reported in Table 3. The standard deviations of the temperature-independent estimate of C_{pm} were obtained directly. The proposed linear temperature dependence of C_{pg} (T) resulted in the temperature-dependent variance

$$s^2(C_{pg})=s^2(C_{pg,0})+s^2(C_{pg,1})T^2+2s(C_{pg,0})s(C_{pg,1})\rho(g_0,g_1)T \tag{14}$$

where $\rho(g_0,g_1)$ is the correlation coefficient between $C_{pg,0}$ and $C_{pg,1}$.

It can be seen (Table 3) that, unlike C_{pm}, the $C_{pg,0}$ and $C_{pg,1}$ estimates were made with relatively high standard deviations. Thus, their individual values are not very significant statistically. On the other hand, the $C_{pg}(T)$ values were obtained with sufficient accuracy in the temperature range studied.

The regression results were verified by comparing the dilatometric T_{g-} values [15] with the minimum values of fictive temperature ($T_{f,H}$(min) in Table 3) obtained from calculations on the cooling DSC curve (Fig. 2). Despite the different cooling rates in the dilatometric experiments and in the DSC cooling curve calculations, it can be deduced from Fig. 2 that the agreement between these two methods of glass transition temperature determination is satisfactory.

The dependence of the heat capacity difference

$$\Delta C_p=C_{pm}-C_{pg}(T_{g-}) \tag{15}$$

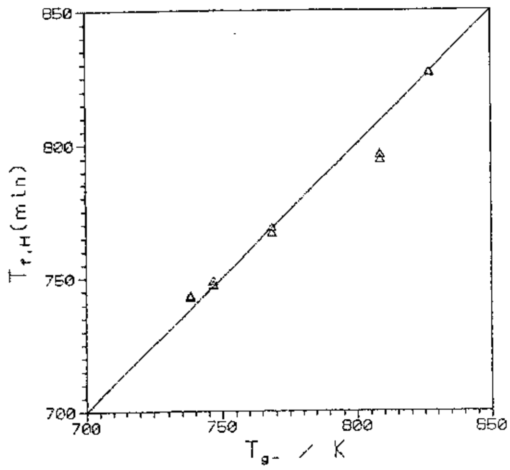

Fig. 2 Correlation between T_{g-} values obtained graphically from the thermodilatometric cooling curve [15], and the computed minimum fictive temperature $T_{f,H}$(min) values

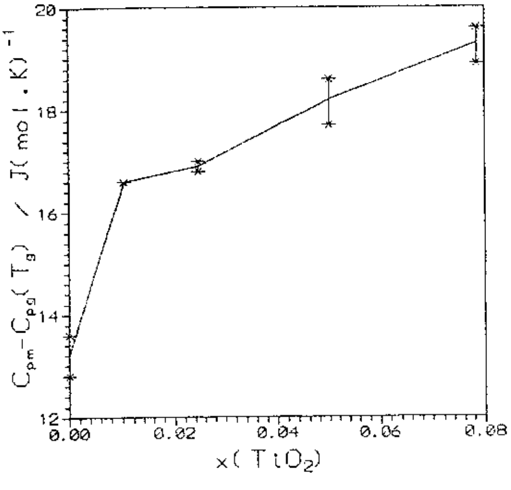

Fig. 3 Dependence of heat capacity difference $C_{pm}-C_{pg}(T_{g-})$ on TiO_2 mole fraction. The broken line is plotted only for the purpose of eye guidance

on the TiO_2 mole fraction is visualized in Fig. 3. The anomalous abrupt increase in this quantity at low TiO_2 contents corresponds well with the experimental calorimetric measurements of Lange and Navrotsky [18]. According to [18], these results can be rationalized either by the changes in the Ti^{4+} coordination number or by the breakdown of alkali titanate complexes.

Some information relating to the structural function of TiO_2 in the title glass series may be obtained from the compositional dependences of the K_H and b re-

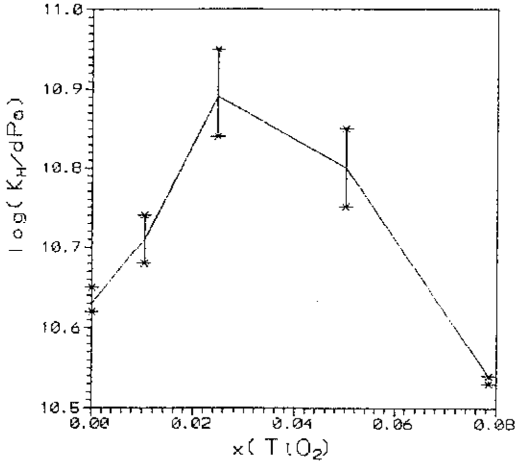

Fig. 4 Dependence of log(K_H/dPa) regression estimates on TiO_2 mole fraction. The broken line is plotted only for the purpose of eye guidance

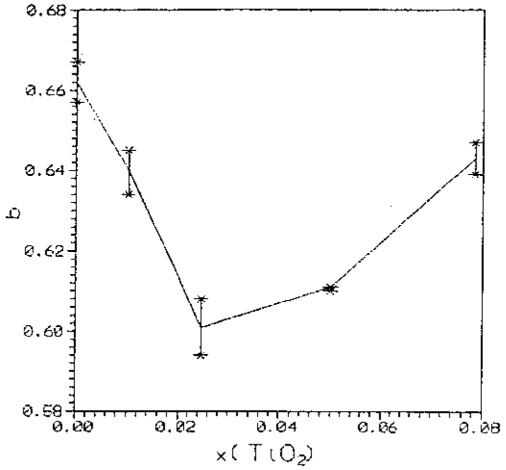

Fig. 5 Dependence of b regression estimates on TiO_2 mole fraction. The broken line is plotted only for the purpose of eye guidance

gression estimates (Figs 4 and 5). When plotted against TiO_2 mole fraction, these quantities displayed similar courses. A significant maximum (minimum) can be observed near a TiO_2 content of 3 mol% for K_H (b). The structural position of TiO_2 changes here, probably in connection with a change in Ti^{4+} coordination number. This result is in accordance with the results of previous work [15] dealing with the viscosity and viscous flow activation energies of the same glass series.

Conclusions

The enthalpic relaxation of the title glasses is well described by the mathematical model used.

The parameters of the relaxation part of the model correlate significantly with the glass composition, indicating a change in Ti^{4+} coordination near a TiO_2 content of 3 mol%.

The values of the minimum fictive temperatures ($T_{f,H}$(min)) obtained during the calculation of the cooling DSC curve correlate well with the cooling thermodilatometric glass transition temperatures (T_{g-})

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