

THERMODILATOMETRY AND STRUCTURAL RELAXATION OF $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ - $\text{Na}_2\text{O} \cdot 2\text{TiO}_2$ GLASSES

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The structural relaxation of title glasses studied by thermodilatometry was well described using the mathematical model based on the stretched exponential relaxation function with relaxation time proportional to instantaneous viscosity. The temperature and fictive temperature dependence of viscosity was expressed by Mazurin's approximation. The obtained relaxation parameters do not correlate significantly with the glass composition. The possible underestimating of regression estimates standard deviations was explained by the experimental data oversampling. The dependencies of equilibrium melt thermal expansion coefficient and glass transition temperature on TiO_2 mole fraction indicate the changes in TiO_2 structural role near the TiO_2 content of 20 mol.%.

INTRODUCTION

It is well known, that titania bearing silicate melts and glasses display unusual behavior of various physical properties [1-3]. These peculiarities may be rationalized in terms of the structural role of TiO_2 , which depends on chemical composition and temperature, namely on its network-forming/modifying character and the changeable oxygen coordination number of Ti^{4+} . Observed temperature and compositional control of various properties may be explained on the basis of homogeneous equilibria between different coordination states of Ti^{4+} in which the other system components, like alkalis and SiO_2 , take part [1,2].

Both the octahedral and tetrahedral coordinations of Ti were found in partially depolymerized sodium titanium silicate glasses by X-ray emission spectroscopy [4]. The X-ray absorption study of Ti-bearing silicate glasses resulted in qualitatively similar results [5]. These results are in agreement with the large positive excess volumes reported by Dingwell [6] in the Na_2SiO_3 - TiO_2 system.

The existence and distribution of various structural motifs in silicate melts and glasses is typically studied by Raman spectroscopy. Unfortunately, unambiguous assignment of Raman bands associated with Ti^{4+} is not possible at this time [2]. On the other hand, the interpretation of results obtained by Henderson and Fleet [3] by micro-Raman spectroscopy is quite different.

Raman spectra of glasses along the Na_2SiO_3 - TiO_2 exhibit no indication of hexacoordinated titanium. Titanium is 4-fold coordinated at low TiO_2 contents, but titanium is predominantly 5-fold coordinated at TiO_2 contents greater than 10 mol.%. Markgraf and Sharma [7] proposed the 5-fold titanium coordination in fresnoite glass on the basis of Raman spectroscopy.

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

The present paper deals with the structural relaxation and thermodilatometry of title glasses. The compositional dependence of the thermal expansion coefficients and parameters of structural relaxation model are studied in reference to the changes of the structural role of TiO_2 .

THEORETICAL PART

Tool [8] and Narayanaswamy's [9] model of structural relaxation describes the hysteresis of thermodilato-

metric curves [10]. The length $l(T, T_{f,l})$ of the sample characterized by thermodynamic temperature T and fictive (structural) temperature $T_{f,l}$ is given by

$$l(T, T_{f,l}) = l(T_r, T_{f,l}) \left[1 + \int_{T_{f,l}}^T \alpha_g(T') dT' + \int_{T_{f,l}}^{T_r} \alpha_m(T') dT' \right] \quad (1)$$

where α_g and α_m are the thermal expansion coefficients of the glass and metastable glass-melt, respectively. The T_r is arbitrary, but a sufficiently high reference temperature. For a given time-temperature schedule $T(t)$ the time dependence of fictive temperature $T_{f,l}(t)$ is obtained from the integral equation

$$T_{f,l}(t) = T(t) \int_0^t dt' \left(\frac{dT}{dt} \right) M_1[\xi(t) - \xi(t')] \quad (2)$$

where M_1 is the relaxation function of dimensionless time ξ that is defined as a time integral of inverse relaxation time τ_1

$$\xi(t) = \int_0^t \frac{dt'}{\tau_1(t')} = \int_0^t \frac{K_1}{\eta(t')} dt' \quad (3)$$

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

$$\tau_1 = \frac{\eta(T, T_{f,l})}{K_1} \quad (4)$$

where the subscript l (length) reflects the dependence of the constant of proportionality K on the particular property studied.

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

$$M_1(\xi) = \exp(-\xi^b) \quad (5)$$

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

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

$$\log \{\eta(T, T_{f,l})\} = A + \frac{B}{T - T_0} \quad (6)$$

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

$$\log \{\eta(T, T_{f,l} = \text{const})\} = A'(T_{f,l}) + B'(T_{f,l})/T \quad (7)$$

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

$$\log \{\eta(T, T_{f,l})\} = \log \{\eta(T_{f,l}, T_{f,l})\} \left(\frac{T_{f,l}}{T} - 1 \right) \quad (8)$$

The time course of the sample length may now be calculated from equations (1) - (8) for arbitrary time-temperature schedule $T(t)$. The dimensionless quantity (sample deformation)

$$\varepsilon(t) = \frac{\Delta l}{l} = \frac{\alpha_{g0} [T(t) - T_{f,l}(t)] + \alpha_{g1} [T(t)^2 - T_{f,l}(t)^2]}{2 + \alpha_m [T_{f,l}(t) - T_r]} \quad (9)$$

is plotted versus temperature in thermodilatometry.

Let us suppose that the A , B , and T_0 parameters of the VFT viscosity equation are known. Then the unknown parameters of the proposed regression model may be estimated using the standard non-linear least squares method, i.e. minimizing the target function

$$F(\alpha_{g0}, \alpha_{g1}, \alpha_1, K_1, \eta_0, b) = \int_0^{t_{\max}} [\varepsilon^{\text{clc}}(t) - \varepsilon^{\text{exp}}(t)]^2 dt \quad (10)$$

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

EXPERIMENTAL PART

Batches were prepared by the mixing of analytical grade purity powdered components - TiO_2 (anatase, Aldrich, 99.9+%), Na_2CO_3 (Lachema, per analysis) and quartz glass (Optical Institute, St.Peterburg). These were melted in a furnace at temperatures between 1500 °C 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 one hour at 600 °C, then the furnace was switched off and the samples remained there until reaching room temperature. The chemical composition of individual samples was determined by colorimetry (TiO_2 , with tiron, i.e. 4,5-Dihydroxy-1,3-Benzene Disulfonic Acid) and emission spectral analysis (Na_2O) after the samples had been

decomposed by HF and H_2SO_4 . The obtained chemical compositions together with the samples numbering convention are summarized in table 1.

Table 1. Chemical compositions of the glass samples (mol.%), and A , B , T_0 of Vogel-Fulcher-Tammann equation (6) [15].

glass	Na_2O	TiO_2	SiO_2^*	A	B (K)	T_0 (K)
T1	33.41	0.00	66.59	2.026	1587.6	593.8
T2	29.65	5.13	65.22	-0.595	2561.2	566.6
T3	32.66	9.92	57.43	-2.927	3410.6	561.0
T4	30.72	15.17	54.12	-1.841	2409.9	629.8
T5	31.08	20.08	48.84	-6.452	4828.5	535.4
T6	34.35	24.07	41.59	-4.537	3524.1	584.6
T8	35.43	33.41	31.16	-5.774	3371.0	612.0
T9	32.79	35.60	31.61	-7.142	3900.6	599.5
T10	33.24	40.20	26.56	-1.061	1380.6	702.3
T43 [†]	33.33	43.00	23.67	-0.939	1434.0	697.8

* - obtained as $100 - \text{Na}_2\text{O} - \text{TiO}_2$

† - as weighted

The thermodilatometric curves were measured by thermomechanical analyzer (Netzsch TMA 402). The samples with only 3 mm height were used to prevent the sample self-deformation above T_g temperature range.

The glass transition temperature T_g was determined from the dilatometric cooling curve recorded on TMA 402 at the cooling rate of 5 K min^{-1} .

RESULTS AND DISCUSSION

The coefficients of VFT viscosity equation (1) of studied glasses (table 1) were taken from our previous work [15].

About 450 experimental $\epsilon^{\text{exp}}(t)$ points were considered in the regression analysis (equation (10)) for all the studied glasses. The details of the regression calculation algorithm used are given elsewhere [16]. The values of Fisher's F-statistics (defined as the ratio of the $\epsilon^{\text{exp}}(t)$ variance to the variance of residuals) and also the values of the standard deviation of approximation s_{appr} presented in table 2 confirms the high accuracy of obtained fits for all the glasses. The comparison of calculated versus experimental $\epsilon(t)$ values is visualised for the best (glass T8) and the worst (glass T4) cases in figures 1 and 2, respectively. It can be seen that the model describes the experimental data with sufficient accuracy in both these border cases.

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

high values of $\log\{\eta_0\}$ standard deviations indicate some ambiguity of this parameter determination, following

Table 2. The parameters of structural relaxation and their standard deviations (in parentheses - e.g. $-17.0(12)$ reads as -17.0 ± 1.2), the values of Fisher's F-statistics, and the standard deviations of approximation s_{appr} .

glass	$\log(K_s/\text{dPa})$	b	$\log(\eta_0/\text{dPa s})$	F	$10^6 \times s_{\text{appr}}$
T1	11.03 (3)	0.467 (9)	-6.4 (7)	28941	21
T2	10.93 (3)	0.510 (18)	-17.0 (12)	15012	30
T3	10.87 (2)	0.527 (9)	-11.9 (5)	29608	24
T4	10.21 (5)	0.543 (24)	-5.4 (11)	7347	61
T5	10.18 (1)	0.659 (8)	-10.7 (4)	27429	28
T6	10.02 (1)	0.569 (8)	-19.1 (6)	22903	31
T8	10.41 (1)	0.588 (5)	-11.9 (3)	69014	22
T9	10.45 (2)	0.545 (7)	-13.6 (5)	30341	34
T10	11.21 (3)	0.493 (7)	-8.1 (6)	24297	55
T43 [†]	10.83 (3)	0.549 (9)	-4.8 (7)	13586	42

from its strong bond to the A coefficient of VFT equation. The A coefficient was determined in our work [15] from relatively narrow range of viscosity values and therefore the individual A values are biased by the strong linear bonds between A , B and T_0 coefficients of VFT equation [17]. That is why the range of $\log\{\eta_0\}$ estimates is very broad without any significant correlation with the glass composition.

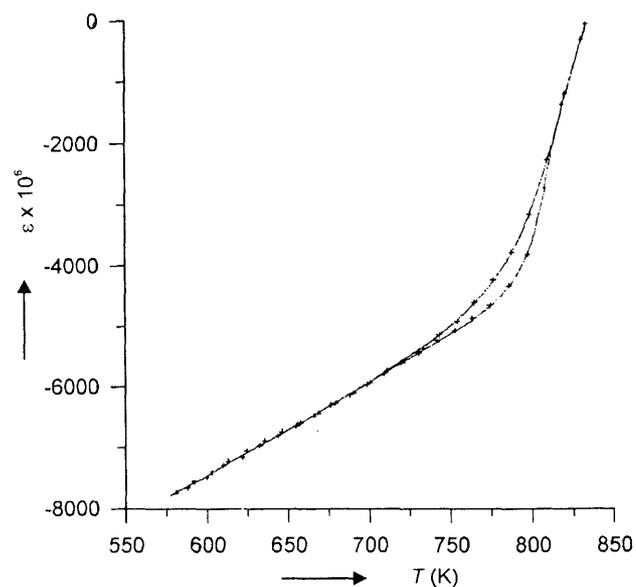


Figure 1. The experimental (cross) points and calculated (solid line) thermodilatometric curves for the T8 glass (Fisher's $F=69014$). Only every tenth experimental point is plotted for simplicity.

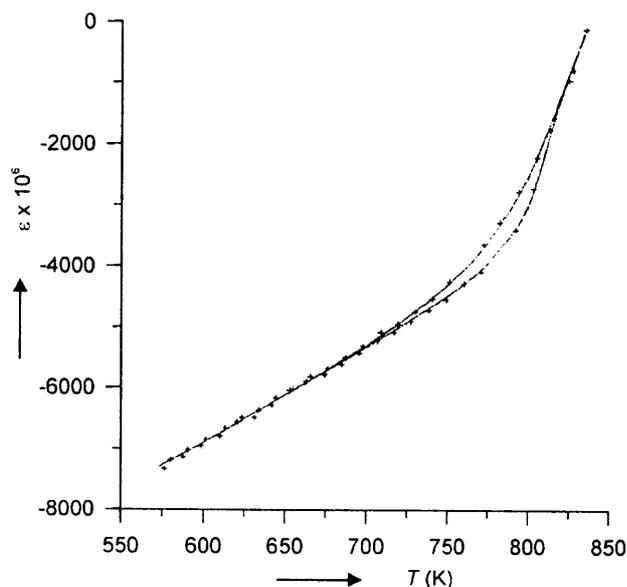


Figure 2. The experimental (cross) points and calculated (solid line) thermodilatometric curves for the T4 glass (Fisher's $F=7347$). Only every tenth experimental point is plotted for simplicity.

The other two relaxation parameters (i.e. K_1 and b) were determined with lower standard deviations. However, like in the case of the η_0 parameter, no significant correlation with the chemical glass composition can be observed for these parameters. Some kind of explanation may be given by supposing that all the relaxation parameters are not directly connected with the glass structure. The assumption, that the accuracy of obtained estimates is not sufficient, seems to be more realistic. Really, the obtained standard deviations of relaxation parameters estimates seem to be unrealistically low. The non-linear least squares method used assumes zero mean measurement errors, zero covariances between measurement errors of various experimental points and,

when the non-weighted sum of squares of deviations is used, constant variances $s^2(\text{exp})$ of measurement errors for all the experimental points, i.e.:

$$E[\epsilon^{\text{exp}}(t_i)] = \epsilon^{\text{clc}}(t_i) \tag{11}$$

and

$$E\{[\epsilon^{\text{exp}}(t_i) - \epsilon^{\text{clc}}(t_i)][\epsilon^{\text{exp}}(t_j) - \epsilon^{\text{clc}}(t_j)]\} = \delta_{i,j} s^2(\text{exp}) \tag{12}$$

where E is the mean value operator, δ is the Kronecker delta, and subscripts i, j denote the experimental points. When "too many" experimental points are taken (i.e. when the sampling frequency is too high) equation (12) is not valid for neighboring experimental points. Such violation of initial assumptions disables the application of least squares method - instead of it the Bayesian estimates have to be used [17]. Thus the absence of correlation between the glass composition and the relaxation parameters may be attributed to the insufficient accuracy of their estimates.

The second subset of estimated parameters of the mathematical model (10) comprises the thermal expansion coefficients of glass α_g and equilibrium melt α_m . The obtained results are summarized in table 3. The standard deviations of temperature independent α_m estimate were obtained directly. The proposed linear temperature dependence of α_g :

$$\alpha_g = \alpha_{g0} + \alpha_{g1} T \tag{13}$$

resulted in the temperature dependent standard deviation:

$$s^2(\alpha_g) = s^2(\alpha_{g0}) + s^2(\alpha_{g1})T^2 + 2s(\alpha_{g0})s(\alpha_{g1}) \rho(\alpha_{g0}, \alpha_{g1})T \tag{14}$$

where $\rho(\alpha_{g0}, \alpha_{g1})$ is the correlation coefficient.

Table 3. The best estimates of thermal expansion coefficients with their standard deviations (e.g. 0.1314(234) reads as 0.1314±0.0234), and the minima of the fictive temperature $T_{f1}(\text{min})$ obtained during the cooling regime.

glass	$10^7 \times \alpha_{g0}$ (K ⁻¹)	$10^7 \times \alpha_{g1}/K^2$ (K ⁻¹)	$\rho(\alpha_{g0}, \alpha_{g1})$	α_m (K ⁻¹)	$T_{f1}(\text{min})$ (K)
T1	80.0 (142)	0.1314 (234)	-0.9995	413.8 (8)	722
T2	89.4 (183)	0.1088 (286)	-0.9996	506.1 (18)	745
T3	93.8 (112)	0.0859 (173)	-0.9995	594.9 (14)	763
T4	93.0 (344)	0.1011 (536)	-0.9996	763.8 (47)	785
T5	31.4 (91)	0.1952 (139)	-0.9994	808.3 (27)	781
T6	100.9 (90)	0.0930 (135)	-0.9993	906.0 (36)	787
T8	76.6 (75)	0.1204 (113)	-0.9994	982.0 (14)	786
T9	108.4 (106)	0.0795 (161)	-0.9993	1015.0 (25)	787
T10	87.8 (132)	0.1040 (200)	-0.9994	1204.6 (46)	785
T43*	47.3 (123)	0.1767 (189)	-0.9992	1027.3 (67)	790

It can be seen (table 3), that unlike the α_m parameter, the α_{g0} and α_{g1} estimates are determined with relatively high standard deviations. Thus their individual values are statistically not very significant. On the other hand, the $\alpha_g(T)$ values are obtained with sufficient accuracy in the temperature range studied. This fact is confirmed by the error bars in Figures 4 and 5 where the $\alpha_g(T)$ values are plotted versus TiO_2 mole fraction for $T = 723 \text{ K}$ and $T = T_g$ temperatures.

Like in the case of relaxation parameters, all the above discussed standard deviations of thermal expansion coefficients are subjected to possible underestimation caused by the oversampling of experimental data (i.e. by assumption (12) violation). Therefore, we have compared the regression estimates of thermal expansion coefficients with their values obtained by using the standard graphical method of thermodilatometric curve analysis [10].

As far as the sample self-deformation was almost completely excluded (by the low sample height, and by the low value of the upper temperature limit of dilatometric loop measurement), the α_m values obtained from the slope of the (above T_g) common part of heating and cooling curve may be considered sufficiently accurate. The comparison of these values with corresponding regression estimates is given in figure 3. For the glass compositions with the TiO_2 content lower than 40 mol.% the results of both methods are identical. The effect of devitrification probably caused the discrepancy that can be seen for the last two glasses with the TiO_2 content of 40 and 43 mol.%.

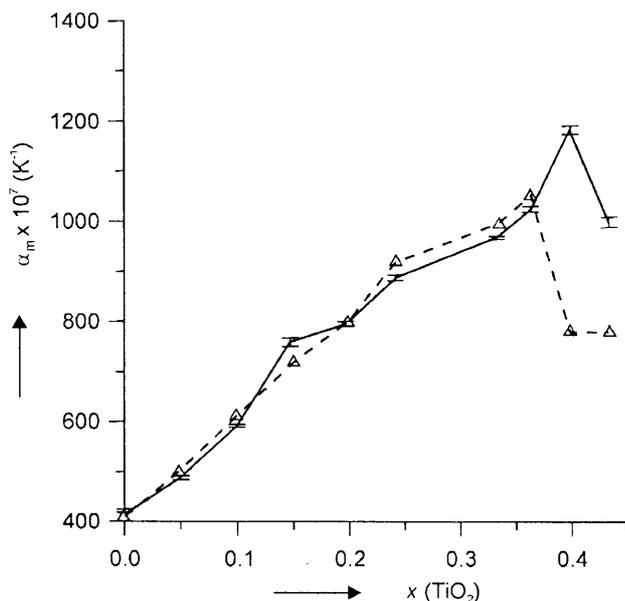


Figure 3. The equilibrium melt thermal expansion coefficients α_m obtained by graphical method (dashed line) and by nonlinear regression analysis (solid line with error bars).

The α_g regression estimates were compared with the graphically obtained ones at various temperatures - at 723 K (figure 4), and at the T_g temperatures that were obtained by cooling curve graphical analysis (figure 5). In the case of $\alpha_g(T_g)$ values (figure 5) both methods give equivalent results (we assume the standard deviations of graphical estimates are close to those of regression esti-

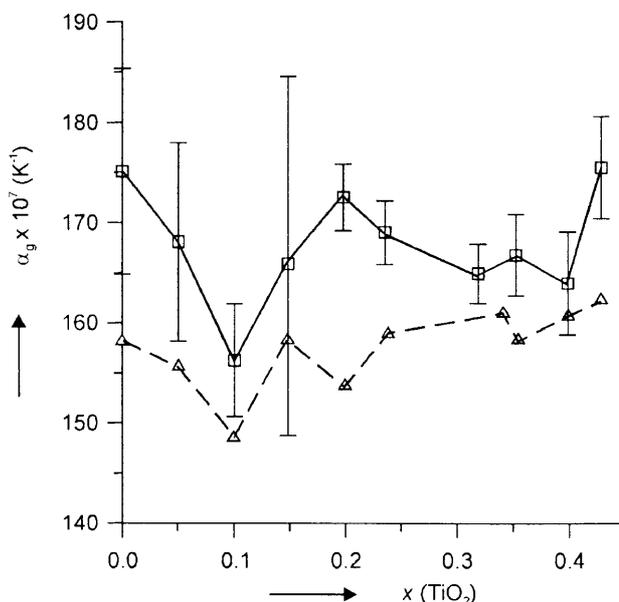


Figure 4. The glass thermal expansion coefficients α_g at 723 K obtained by graphical method (dashed line) and by nonlinear regression analysis (solid line with error bars).

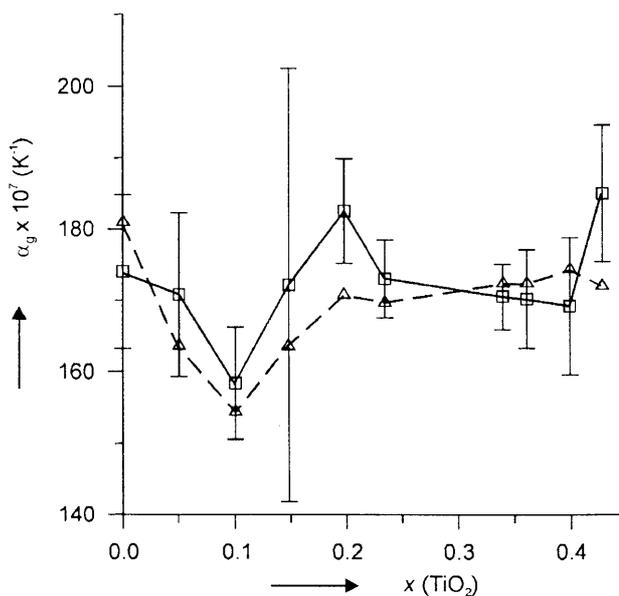


Figure 5. The glass thermal expansion coefficients α_g at T_g obtained by graphical method (dashed line) and by nonlinear regression analysis (solid line with error bars).

mates). On the other hand, the regression estimates of $\alpha_g(723\text{ K})$ are slightly higher than the corresponding graphical values. This small discrepancy may be attributed to graphical method, where the $\alpha_g(723\text{ K})$ values were obtained from least squares linearization of "arbitrary" chosen part of the dilatometric curve near the 723 K point.

The last test of regression results was performed comparing the T_g values with the minimum values of fictive temperature ($T_{fi}(\text{min})$ in table 3) attained in calculating the cooling dilatometric curve (figure 6). It can be deduced from figure 6, that the agreement of both these methods for glass transition temperature determination is fully satisfactory.

Some information related to the TiO_2 structural function in title glass series may be obtained only from the α_m and T_g values. Both these quantities, when they are plotted against TiO_2 mole fraction, showed similar course with significant change of slope near the 20 mol.% of TiO_2 . Here the network-forming function of TiO_2 vanishes, probably in connection with the change of Ti^{4+} coordination number. This result is in agreement with the results of our previous work [15] dealing with the viscosity and viscous flow activation energies of the same glass series. Also the Raman study of the same glass series [2] showed that near 20 mol.% of TiO_2 the tetrahedral TiO_4 coordination reaches its maximum value.

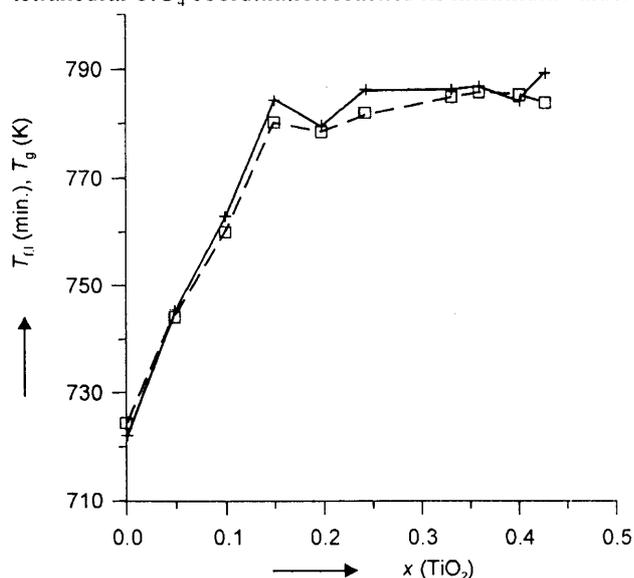


Figure 6. The T_g values obtained by graphical method from the dilatometric cooling curve and the computed minimum fictive temperature $T_{fi}(\text{min})$ values.

CONCLUSIONS

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

The parameters of the relaxation part of the used model are not significantly correlated with the glass composition, probably because of insufficient accuracy of their determination.

The extraordinarily low values of standard deviations of regression estimates of some parameters were caused by the oversampling of experimental data.

The dependencies of melt thermal expansion coefficient and glass transition temperature on TiO_2 mole fraction indicate the changes in TiO_2 structural role near the TiO_2 content of 20 mol.%. This result is in agreement with the results of other works [2,15].

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References

1. Mysen B.O.: *Structure and properties of silicate melts*. Vol.4, *Developments in geochemistry*. Elsevier, New York 1988.
2. Mysen B.O., Neuville D.: *Geochim. Cosmochim. Acta* 59, 325 (1995).
3. Henderson G.H., Fleet M.E.: *The Canadian Mineralogist* 33, 399 (1995).
4. Hanada T., Soga N.: *J. Non-Cryst. Solids* 38&39, 105 (1980).
5. Dingwell D.B., Paris E., Seifert F., Mottana A., Romano C.: *Phys. Chem. Minerals* 21, 501 (1994).
6. Dingwell D.B.: *Geochim. Cosmochim. Acta* 56, 3403 (1992).
7. Markgraf S.A., Sharma S.K.: *J. Am. Ceram. Soc.* 75, 2630 (1992).
8. Tool A.Q.: *J. Am. Ceram. Soc.* 29, 240 (1946).
9. Narayanaswamy O.S.: *J. Am. Ceram. Soc.* 54, 491 (1971).
10. Mazurin O.V.: *Steklovanie*. Nauka, Leningrad 1986. (In Russian).
11. Rekhson S.M., Bulaeva A.V., Mazurin O.V.: *Sov. J. Inorg. Mater.* 7, 622 (1971) (English transl.).
12. Williams G., Watts D.C., Dev B.S., North A.M.: *Trans. Faraday Soc.* 67,1323 (1971).
13. Mazurin O.V.: In: *Glass: science and technology*. Vol. 3, *Viscosity and relaxation*, (Ed. D.R.Uhlmann and N.J.Kreidl), pp.119-180, Academic Press, London 1986.
14. Mazurin O.V., Klyuev V.P., Stolyar S.V.: *Glastechn. Ber.* 56K, 1148 (1983).
15. Liška M., Klyuev V.P., Antalík J., Štubňa I.: *Phys. Chem. Glasses* (to be published).
16. Liška M., Štubňa I., Antalík J., Perichta P.: *Ceramics-Silikáty* 40, 15 (1996).
17. Brad Y.: *Nonlinear parameter estimation*, Academic Press, New York 1974.

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TERMODILATOMETRIA A ŠTRUKTÚRNA RELAXÁCIA
 $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ - $\text{Na}_2\text{O} \cdot 2\text{TiO}_2$ SKIEL

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Štruktúrne relaxácia skúmaných $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ - $\text{Na}_2\text{O} \cdot 2\text{TiO}_2$ skiel (Tab.1) dobre opísal (Obr.1, 2) matematický model (1-9)

založený na Kohlrauschovej Williamsovej Wattsovej relaxačnej funkcii (3, 5) s relaxačnými časmi τ_i priamo úmernými okamžitej viskozite (4). Závislosť dynamickej viskozity od štruktúrnej ($T_{r,i}$) a termodynamickej (T) teploty sa vyjadrila Vogelovou Fulcherovou Tammanovou viskozitnou rovnicou (6) a Mazurinovou aproximáciou (7, 8). Získané relaxačné parametre (Tab.2) nevykázali štatisticky významnú koreláciu so zložením skúmaných skiel. Pravdepodobné podhodnotenie smerodajných odchýlok regresného modelu (9) spôsobilo prevzorkovanie experimentálnych dát a tým porušenie podmienky (12) aplikácie použitej metódy najmenších štvorcov. Závislosti koeficientu teplotnej rozťažnosti metastabilnej rovnovážnej taveniny a hodnoty teploty skelného prechodu od obsahu TiO_2 indikovali (v súlade s predchádzajúcimi prácami) zmenu štruktúrnej funkcie TiO_2 v oblasti obsahu 20 mol. %.