

# HEAT CAPACITIES OF 15Na<sub>2</sub>O·10(MgO, CaO, TiO<sub>2</sub>, ZrO<sub>2</sub>)·75SiO<sub>2</sub> GLASSES

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## Abstract

Heat capacities  $C_p$  of title glasses were measured for temperature ranging from 50 to 550°C. True linear temperature dependences were observed for all studied glasses at temperatures sufficiently lower than the glass transition temperature. The temperature-compositional  $C_p$  dependence was described by the linear model with only statistically significant coefficients retained. The parameters were estimated using the standard least squares procedure. The results obtained may be used for evaluation of viscosity values according to Adam and Gibbs theory.

**Keywords:** glasses, heat capacity, linear model

## Introduction

The knowledge of heat capacity-temperature-composition dependence represents the substantial prerequisite for calculation of configuration entropy and viscosity as well. According to the theory of Adam and Gibbs the configurational entropy  $S_c$  determines the temperature  $T$  dependence of viscosity [1-3]

$$\eta = \eta_0 \exp \left( \frac{\Delta\mu S_c^*}{kTS_c} \right) \quad (1)$$

where  $k$  is the Boltzman's constant,  $\Delta\mu$  is the potential barrier per molecule hindering rearrangement and  $S_c^*$  is the configurational entropy of the smallest cooperatively rearranging subsystem.

It is generally assumed that the latter must contain two configurations, so  $S_c^* = k \cdot \ln 2$ . For the configurational entropy it can be written [4, 5]

$$S_c = \int_{T_K}^T \frac{\Delta C_p}{T} dT \quad (2)$$

where  $T_K$  is the so called Kauzmann's [4] temperature, for which holds  $S_c(T_K) = 0$  and  $\Delta C_p$  is the difference between the heat capacities of the meta-stable liquid  $C_{pl}$  and corresponding glass  $C_{pg}$ , respectively.

Thus the knowledge of compositional dependence of heat capacities allows (at least theoretical) to calculate the temperature-compositional glass viscosity curve.

Moreover the tight binding between the configurational molar entropy and the shape of coordination polyhedron may serve as efficient tool for the glass structure investigation [5, 6].

The present work describes the functional dependence between the heat capacity on the one hand and the temperature and chemical composition on the other in the title series of titanium bearing alkali-resistant glasses.

## Experimental part

Batches were prepared from glass sand, zirconium silicate and chemically pure  $TiO_2$ ,  $Na_2CO_3$ ,  $MgCO_3$  and  $CaCO_3$  and melted in a furnace at temperatures between 1500–1550°C in a 10%Rh–Pt crucible. Homogeneity was ensured by repeated fritting and hand-mixing of the glass during melting. Each melt was poured from the crucible onto a stainless steel plate. Then were the samples tempered in a muffle furnace for one hour at 600°C, after which the furnace was switched off and samples were allowed to remain there until completely cool [7, 8].

The chemical composition of individual samples was determined by ICP emission spectral analysis after the samples had been decomposed by melting with lithium tetraborate (Table 1).

Heat capacities of powdered samples were measured by standard DSC procedure in the temperature range of 50–550°C using the Perkin Elmer DSC-7 scanning calorimeter.

## Computational method

The problem we deal with is one of the special cases of property–temperature–composition relationships regression analysis. As far as the partial temperature–property (at constant composition) dependences are often described by the formal equations with many linearly interdependent parameters there is important to elucidate the general strategy of pertinent regression treatment.

Let us suppose the dependence of property  $\gamma$  on composition  $\vec{x}$  and temperature  $T$  in the form

$$\hat{\gamma}(\vec{x}, T) = f[\vec{\theta}(\vec{x}), T] \quad (3)$$

where the parameters  $\vec{\theta}$  are only composition dependent.

**Table 1** Compositions (mol%) of the studied glasses

<i>i</i>	Na <sub>2</sub> O	CaO	MgO	ZrO <sub>2</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>
1	14.55	0	0	0	9.26	76.19
2	15.35	0	0	9.78	0	74.87
3	15.13	5.20	0	5.09	0	74.58
4	14.69	5.23	0	0	4.90	75.18
5	14.92	0	0	4.59	4.82	75.67
6	14.40	3.20	0	3.20	3.50	75.80
7	14.74	0	0	7.73	2.39	75.14
8	14.61	2.55	0	4.61	2.15	76.08
9	15.04	2.34	0	2.13	4.70	75.79
10	14.43	0	9.57	0	0	75.99
11	14.54	0	5.40	0	6.06	74.00
12	14.72	0	5.27	5.02	0	74.99
13	14.79	2.62	7.58	0	0	75.01
14	15.01	0	7.94	2.55	0	74.50
15	15.02	0	2.73	7.61	0	74.65
16	14.26	5.36	2.54	0	2.48	75.36
17	14.80	2.71	2.71	0	5.25	74.53
18	14.45	2.77	5.33	0	2.54	74.91
19	14.79	0	4.58	2.50	2.39	75.75

The best estimate of unknown parameters  $\vec{\theta}$  may be obtained by minimization of the weighted sum of squared deviations between the calculated and (mutually independent) measured values of  $y(\vec{x}_i, T_{ij})$

$$U_0 [\hat{\vec{\theta}}(\vec{x}_1), \hat{\vec{\theta}}(\vec{x}_2), \dots, \hat{\vec{\theta}}(\vec{x}_M)] = \sum_i^M \sum_j^{N_i} w_y(\vec{x}_i, T_{ij}) [\hat{y}(\vec{x}_i, T_{ij}) - y(\vec{x}_i, T_{ij})]^2 = \min \quad (4)$$

where the weighting coefficients  $w_y$  are indirectly proportional to the variances of corresponding experimental values.

$$w_y(\vec{x}_i, T_{ij}) \approx \frac{1}{s^2 [y(\vec{x}_i, T_{ij})]} \quad (5)$$

The optimization task (4) may be decomposed into the file of simple minimizations for distinct compositions

$$U_{\theta} [\hat{\theta}(\vec{x}_i)] = \sum_j^{N_i} w_{y_j}(\vec{x}_i, T_{ij}) [\hat{y}(\vec{x}_i, T_{ij}) - y(\vec{x}_i, T_{ij})]^2 = \min, \quad i = 1, 2, \dots, M \quad (6)$$

Let us suppose the compositional dependence  $\hat{\theta}(\vec{x})$  in the form

$$\hat{\theta}(\vec{x}) = \vec{g}(\vec{p}, \vec{x}) \quad (7)$$

where  $\vec{p}$  denotes the vector of unknown parameters. The best unbiased estimate of these parameters  $\hat{\vec{p}}$  may be obtained by minimization of the target function

$$U_p(\hat{\vec{p}}) = \sum_i^M [\vec{g}(\hat{\vec{p}}, \vec{x}_i) - \hat{\theta}(\vec{x}_i)]^T W_{\theta}(\vec{x}_i) [\vec{g}(\hat{\vec{p}}, \vec{x}_i) - \hat{\theta}(\vec{x}_i)] = \min \quad (8)$$

where  $W_{\theta}(\vec{x}_i) = [V_{\theta}(\vec{x}_i)]^{-1}$  is the inverse of the covalence matrix defined by

$$V_{\theta}(\vec{x}_i) = E \left\{ [\hat{\theta}(\vec{x}_i) - E[\hat{\theta}(\vec{x}_i)]] [\hat{\theta}(\vec{x}_i) - E[\hat{\theta}(\vec{x}_i)]]^T \right\} \quad (9)$$

here  $E$  denotes the mean value operator.

To overcome the complexity of the minimization task (8) we prefer to solve the following broader but simpler task

$$U_y(\hat{\vec{p}}) = \sum_i^M \sum_j^{N_i} w_{y_j}(\vec{x}_i, T_{ij}) \left\{ f[\vec{g}(\hat{\vec{p}}, \vec{x}_i), T_{ij}] - y(\vec{x}_i, T_{ij}) \right\}^2 = \min \quad (10)$$

## Results and discussion

The powdered character of samples was reflected in artifacts on the DSC curves near the glass transition temperature  $T_g$ . On the other hand, all temperature dependences of measured heat capacities were practically linear in the low temperature range. The linear character of obtained DSC curves were in all cases statistically confirmed by Student's  $t$ -tests of statistical significance of coefficients of following equation

$$C_p(T) = a + bT + cT^2 + dT^{-2} \quad (11)$$

Only the  $a$  and  $b$  coefficients were found as non-zero at the 99% significance level. Many authors have carried out similar data fits, e.g. Richet *et al.* [5] for silicate glasses at temperatures above 70 K. The compositional dependence of  $a$  and  $b$  coefficients of above equation may be therefore expressed as follows

$$a = a_0 + a_1(\text{CaO}) + a_2(\text{ZrO}_2) + a_3(\text{TiO}_2) \quad (12a)$$

$$b = b_0 + b_1(\text{CaO}) + b_2(\text{ZrO}_2) + b_3(\text{TiO}_2) \quad (12b)$$

The nearly constant values of  $x(\text{SiO}_2) = 0.75$  and  $x(\text{Na}_2\text{O}) = 0.15$  (Table 1) and the  $x(\text{MgO})$  value bonded by the following material balance equation.

$$x(\text{MgO}) + x(\text{CaO}) + x(\text{ZrO}_2) + x(\text{TiO}_2) = 0.1 \quad (13)$$

were omitted from the Eqs (12a) and (12b). Relating to the Eq. (7) the vector of unknown parameters may be now explicitly written as

$$p \equiv \{a_0, a_1, a_2, a_3, b_0, b_1, b_2, b_3\} \quad (14)$$

The values of  $a_i$ ,  $b_i$  ( $i = 0, 1, 2, 3$ ) were determined by the standard least squares procedure using the target function (8). The optimal form approximation equation was obtained by stepwise excluding of statistically non-significant parameters from the starting full form of Eq. (11).

The resulting optimal fit is characterized by the distribution of normalized deviations (i.e. of the deviations between the calculated and experimental point

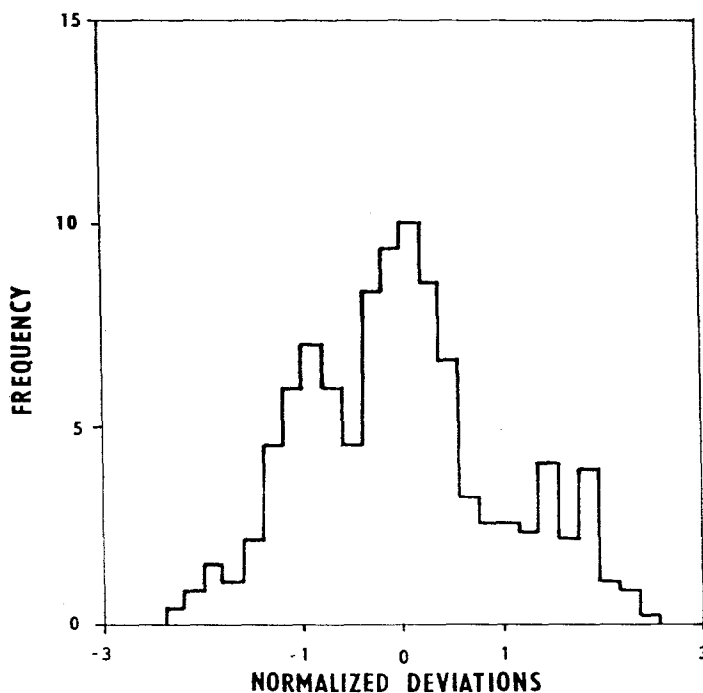


Fig. 1 Frequency diagram of normalized deviations between experimental and calculated heat capacities

**Table 2** Coefficients of approximation polynomials (12), their standard deviations  $s$  and Students  $t$  - statistics

Coefficient	$y_i$		$s(y_i)$		$t(y_i)$
$a_0$	30.5	$\text{J mol}^{-1} \text{K}^{-1}$	0.91	$\text{J mol}^{-1} \text{K}^{-1}$	33
$b_0$	0.0601	$\text{J mol}^{-1} \text{K}^{-2}$	0.0023	$\text{J mol}^{-1} \text{K}^{-2}$	26
$b_1$	0.066	$\text{J mol}^{-1} \text{K}^{-2}$	0.015	$\text{J mol}^{-1} \text{K}^{-2}$	4.2
$b_2$	0.079	$\text{J mol}^{-1} \text{K}^{-2}$	0.012	$\text{J mol}^{-1} \text{K}^{-2}$	6.7
$b_3$	0.163	$\text{J mol}^{-1} \text{K}^{-2}$	0.013	$\text{J mol}^{-1} \text{K}^{-2}$	13

divided by standard deviation of approximation) in Fig. 1. At 462 degrees of freedom (i.e. 467 experimental points minus 5 non-zero  $a_i$ ,  $b_i$  values) the resulting standard deviation of approximation has the value of  $s_a = 2.6 \text{ J (mol K)}^{-1}$ . The best estimates of  $a_i$ ,  $b_i$  coefficients are together with corresponding standard deviations and Student's  $t$ -values summarized in Table 2.

Comparing the obtained  $C_p(\vec{x}, T)$  function with those constructed on the basis of linear approximation of the pure oxides  $C_p$ 's [9] we can deduce that the most significant discrepancies relates to  $\text{TiO}_2$  oxide. This is in good harmony with the fact that  $\text{Ti}^{4+}$  changes its coordination (from  $\text{TiO}_4$  to  $\text{TiO}_6$ ) and role (from network-former to network-modifier) in the studied glass compositional range [7, 8, 10, 11].

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