# PHYSICAL PROPERTIES AND CHEMICAL DURABILITY OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES

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*Density, thermal expansion, glass transition temperature, refractive index, molar refractivity and chemical durability of five- and six-component glasses with as weighted composition $xNa_2O{\cdot}(15\text{-}x)K_2O{\cdot}yCaO{\cdot}(10\text{-}y)ZnO{\cdot}zZrO_2{\cdot}(75\text{-}z)SiO_2$ (x = 0, 7.5, 15; y = 0, 5, 10; z = 5, 7) were measured. The obtained experimental data were merged together with the previous results obtained for analogous glasses with lower zirconia content. The full set of glasses enabled the quantitative statistical estimation of possible mixed-oxide effects. The results of the multilinear regression analysis pointed out the ideal behavior of molar volume and molar refractivity. The strongest influence of mutual oxide interactions was found for chemical durability and glass transition temperature. The regression analysis of compositional dependence of metastable melt thermal expansion coefficient practically failed. The need of property-composition study based on the thermodynamic model was pointed out. Qualitatively the obtained results confirmed those previously obtained for the analogous glasses with zirconia content reaching up to 3 mol. %.*

## INTRODUCTION

The property-composition relationships of $x\mathrm{Na_2O}{\cdot}{\cdot}(15\text{-}x)\mathrm{K_2O}{\cdot}y\mathrm{CaO}{\cdot}(10\text{-y})\mathrm{ZnO}{\cdot}z\mathrm{ZrO_2}{\cdot}(75\text{-}z)\mathrm{SiO_2}$ ($x$ = 0, 7.5, 15; y =0, 5, 10; z = 0, 1, 3) glasses and glass melts were studied in our previous work [1-4]. The reason for this study was the extraordinary importance of this glass system for glass technology, namely for Portland cement composites and for the replacement of toxic oxides (barium oxide, lead oxide) in crystal glass in order to minimize the impact of glass production on the environment, to minimize health hazards of the product, and to increase its dishwashing resistance [5-9]. In our previous work [1-4] the five- and six-component glasses were studied only with low zirconia content reaching up to 3 mol. %. From this point of view the present paper extends the previous work up to 7 mol. % of zirconia. In the previous work the network strengthening effect of $ZrO_2/SiO_2$ and ZnO/CaO equimolar substitutions was demonstrated. Simultaneously the effect of $K_2O/Na_2O$ substitution was identified leading to increase of the thermal expansion coefficients, glass transition temperature, molar volume, refractive index accompanied with significant decrease of chemical durability. However for quantitative estimation and mathematical description of glass composition - property relationships the significant influence of mutual oxide interactions was identified [3]. From this point of view the need of experimental data of five- and six-component glasses with higher zirconia content was identified. Simultaneously, with these experimental data absent, the statistically robust estimation of zirconia content influence on the effect of ZnO/CaO and $K_2O/Na_2O$ equimolar substitutions was not possible. Moreover, the regression treatment presented in our previous work [3] was based on the theoretical - as weighted - glass compositions. The glass compositions determined by the ICP OES spectral analysis are used for the multilinear regression treatment and the detailed analysis of correlation matrix between independent variables is used before constructing the regression model in the present work.

## EXPERIMENTAL

The glass batches were prepared by mixing of powdered carbonates and oxides $Na_2CO_3$ (AFT, p.a.), $K_2CO_3$ (Fluka, p.a.), $CaCO_3$ (AFT, p.a.), ZnO (Fluka, p.a.), $ZrSiO_4$ (Aldrich, p.a.), $SiO_2$ (AFT, min. 96.5 %). Sodium sulphate (AFT, p.a.) and potassium sulphate (Lachema, p.a.) were used as fining agents. Glasses were melted in Pt-10%Rh crucible in superkanthal furnace at temperature of 1600°C for two-three hours in ambient atmosphere. The homogeneity was ensured by repeated hand mixing of the melt. The glass melt was then poured onto a stainless steel plate. The samples were tempered in a muffle furnace for one hour at 650°C, after which the furnace was switched off and samples allowed remain there until completely cool.

The chemical composition of studied glasses was determined after their decomposition by the mixture of HF and $HClO_4$ by inductively coupled plasma optical emission spectroscopy (VARIAN - Vista MPX/ICP-OES). The content of $SiO_2$ has not been analyzed.

Table 1. The composition and abbreviation of studied glasses (mol.%) [1-3], the glasses synthesized in the present work are summarized in the bottom part.

| Glass | $Na_2O$ | $K_2O$ | CaO | ZnO | $ZrO_2$ | $SiO_2$ |
|---|---|---|---|---|---|---|
| NCZ0 | 15.30 | 0 | 9.22 | 0 | 0 | 75.48 |
| NCZ1 | 13.86 | 0 | 10.69 | 0 | 0.93 | 74.52 |
| NCZ3 | 13.42 | 0 | 10.19 | 0 | 2.86 | 73.53 |
| NCZ5 | 14.99 | 0 | 10.00 | 0 | 4.87 | 70.14 |
| NCZ7 | 14.07 | 0 | 9.78 | 0 | 6.77 | 69.38 |
| KCZ0 | 0 | 14.98 | 8.42 | 0 | 0 | 76.60 |
| KCZ1 | 0 | 14.29 | 8.44 | 0 | 1.02 | 76.25 |
| KCZ3 | 0 | 15.41 | 10.08 | 0 | 3.28 | 71.23 |
| KCZ5 | 0 | 15.44 | 10.06 | 0 | 4.92 | 69.58 |
| NzZ0 | 14.80 | 0 | 0 | 9.90 | 0 | 75.30 |
| NzZ1 | 15.04 | 0 | 0 | 9.41 | 1.03 | 74.52 |
| NzZ3 | 15.29 | 0 | 0 | 11.04 | 3.19 | 70.48 |
| NzZ5 | 14.77 | 0 | 0 | 9.01 | 4.90 | 71.32 |
| NzZ7 | 14.18 | 0 | 0 | 9.89 | 6.54 | 69.39 |
| KzZ0 | 0 | 15.74 | 0 | 8.47 | 0 | 75.79 |
| KzZ1 | 0 | 14.93 | 0 | 10.49 | 0.97 | 73.61 |
| KzZ3 | 0 | 14.20 | 0 | 9.86 | 2.80 | 73.14 |
| KzZ5 | 0 | 16.00 | 0 | 10.44 | 4.91 | 68.65 |
| NKCZ1 | 7.64 | 7.36 | 8.61 | 0.00 | 0.95 | 75.44 |
| NKzZ1 | 7.45 | 7.41 | 0.00 | 10.08 | 0.98 | 74.08 |
| NCzZ1 | 13.51 | 0.00 | 4.80 | 4.58 | 0.89 | 76.22 |
| KCzZ1 | 0.00 | 15.81 | 5.03 | 5.27 | 1.01 | 72.88 |
| NKCzZ1 | 8.22 | 8.01 | 4.40 | 5.40 | 1.05 | 72.92 |
| NKCZ3 | 7.54 | 7.44 | 8.84 | 0 | 2.86 | 73.32 |
| NKzZ3 | 7.30 | 7.06 | 0 | 9.63 | 2.61 | 73.40 |
| NCzZ3 | 13.72 | 0 | 4.72 | 5.01 | 2.71 | 73.84 |
| KCzZ3 | 0 | 13.95 | 4.47 | 4.95 | 2.66 | 73.97 |
| NKCzZ3 | 6.61 | 6.96 | 4.41 | 4.81 | 2.58 | 74.63 |
| NKCZ5 | 7.74 | 6.89 | 9.97 | 0 | 5.12 | 70.28 |
| NKzZ5 | 7.66 | 7.13 | 0 | 10.92 | 5.22 | 69.07 |
| NCzZ5 | 15.78 | 0 | 5.13 | 5.58 | 5.42 | 68.09 |
| KCzZ5 | 0 | 13.64 | 4.97 | 5.48 | 5.20 | 70.72 |
| NKCzZ5 | 7.82 | 7.18 | 5.18 | 5.63 | 5.35 | 68.85 |
| NKCZ7 | 7.66 | 7.01 | 9.98 | 0 | 7.18 | 68.17 |
| NKzZ7 | 7.83 | 7.00 | 0 | 11.03 | 7.54 | 66.60 |
| NCzZ7 | 15.78 | 0 | 5.11 | 5.43 | 7.40 | 66.29 |
| KCzZ7 | 0 | 13.88 | 4.98 | 5.43 | 7.25 | 68.46 |
| NKCzZ7 | 7.86 | 6.99 | 5.00 | 5.53 | 7.40 | 67.22 |

Chemical composition of studied silicate glasses is summarized together with the composition of glasses studied in our previous work in Table 1.

The density of glass at laboratory temperature was measured by Archimedes method by dual weighting of glass sample in air and in distilled water. Refractive index, $n_D^{20}$, was measured on polished prismatic glass samples by Abbe's refractometer at 20°C. Chemical durability against water, *CD*, was determined on grained sample according to the norm STN ISO 70 0531 at 98°C. The *CD* is expressed as the amount of 0.01 M HCl needed for neutralization of alkalis leached from the glass. Thus lower *CD* value means better chemical durability.

Thermodilatometric experiments were performed on TMA Q400 EM vertical dilatometer on prismatic samples with dimensions of (5 × 5 × 20) mm$^3$. Thermal expansion coefficient of glass, $a_g$, and metastable melt, $a_m$, together with the glass transition temperature, $T_g$, were obtained by cooling from sufficiently high temperature by the cooling rate of 5°C.min$^{-1}$. The linear thermal expansion coefficients of glass, $a_g$, and metastable, $a_m$, melt were estimated from the slope of the cooling curve in temperature ranges of (623-723) K and (913-1063) K, respectively. The glass transition temperature, $T_g$, was determined from the position of the intersection of two lines (with the respective slopes of $a_g$ and $a_m$).

The molar refractivity, $R_m$, was calculated by:

$$R_m = \frac{\left(n_D^{20}\right)^2 - 1}{\left(n_D^{20}\right)^2 + 2} \frac{\overline{M}_g}{\rho^{20}} \qquad (1)$$

where $n^{20}{}_D$ is the refractivity index of glasses at laboratory temperature at wavelength 589.3 nm. $\overline{M}_g$ is the average molar (formula) weight of glass:

$$\begin{aligned}\overline{M}_g &= x(Na_2O)M(Na_2O) + x(K_2O)M(K_2O) + \\ &+ x(CaO)M(CaO) + x(ZnO)M(ZnO) + \\ &+ x(ZrO_2)M(ZrO_2) + x(SiO_2)\end{aligned} \qquad (2)$$

where $x(i)$ is the mole fraction and $M(i)$ is the molar weight of oxide $i$. The molar volume, $V_m$, was calculated by:

$$V_m = \frac{\overline{M}_g}{\rho} \qquad (3)$$

## RESULTS AND DISCUSSION

The obtained experimental results are summarized in Table 2. Together with ten five- and six-component glasses with the $ZrO_2$ content of 5 and 7 mol.% synthesized in the present work the experimental results obtained for 28 analogous glasses in our previous work are reported. The compositional range reported forms sufficient basis for multilinear analysis estimation of possible mixed - oxide effects for various property - composition relationships. The general regression model including only the interaction terms between mutually substituted oxides (i.e. $Na_2O$–$K_2O$, CaO–ZnO, $ZrO_2$–$SiO_2$) up to the second order can be written in the form:

$$p(\vec{x})\ a_0 + a(Na_2O)x(Na_2O) + a(K_2O)x(K_2O) + a(CaO)x(CaO) + a(ZnO)x(ZnO) + a(ZrO_2)x(ZrO_2) + a(SiO_2)x(SiO_2) + a(Na_2O, Na_2O)x^2(Na_2O) + a(K_2O, K_2O)x^2(K_2O) + a(CaO, CaO)x^2(CaO) + a(ZnO, ZnO)x^2(ZnO) + a(ZrO_2, ZrO_2)x^2(ZrO_2) + a(SiO_2, SiO_2)x^2(SiO_2) + a(Na_2O, K_2O)[x(Na_2O)\,x(K_2O)] + a(CaO, ZnO)[x(CaO)\,x(ZnO)] + a(ZrO_2, SiO_2)[x(ZrO_2)x(SiO_2)] \quad (4)$$

where $p$ stands for $n_D^{20}$, $\rho$, $V_m$, $R_m$, $CD$, $a_g$, $a_m$, and $T_g$, respectively. We can introduce some short notation:

$$p(\vec{\xi}) = a_0 + \sum_{i=1}^{15} a_i \xi_i \quad (5)$$

where $a_1 = a(Na_2O)$, $\xi_1 = x(Na_2O)$, …, $a_{15} = a(ZrO_2,SiO_2)$, $\xi_{15} = x(ZrO_2)x(SiO_2)$.

The above regression equation contains 15 independent variables, $a_i$, plus an absolute term $a_0$. Before using this equation the correlation analysis was performed to find the mutually strongly correlated independent variables (Table 3). First we can see that the result of the correlation analysis reflects the theoretical compositions of the studied glasses, i.e. the $Na_2O$–$K_2O$, CaO–ZnO,

Table 2. Measured properties of studied glasses [1-3], glasses synthesized in the present work are summarized in the bottom part.

| Glass | $\rho \pm 0.001$ (g/cm$^3$) | $V_m \pm 0.05$ (cm$^3$/mol) | $n_D \pm 0.001$ | $R_m$ (cm$^3$/mol) | $10^7 \times a_g \pm 3$ (K$^{-1}$) | $10^7 \times a_m \pm 5$ (K$^{-1}$) | $T_g \pm 1$ (K) | $CD \pm 0.02$ (ml) |
|---|---|---|---|---|---|---|---|---|
| NCZ0 | 2.475 | 24.24 | 1.514 | 7.299 | 95 | 357 | 807 | - |
| NCZ1 | 2.506 | 24.14 | 1.519 | 7.332 | 96 | 320 | 830 | 0.69 |
| NCZ3 | 2.572 | 24.00 | 1.532 | 7.437 | 94 | 292 | 850 | 0.29 |
| NCZ5 | 2.643 | 23.85 | 1.546 | 7.556 | 85 | 255 | 867 | 0.23 |
| NCZ7 | 2.702 | 23.77 | 1.560 | 7.684 | 87 | 325 | 907 | 0.17 |
| KCZ0 | 2.478 | 26.17 | 1.516 | 7.907 | 103 | 330 | 860 | - |
| KCZ1 | 2.489 | 26.22 | 1.519 | 7.960 | 102 | 263 | 883 | 1.33 |
| KCZ3 | 2.573 | 26.04 | 1.535 | 8.110 | 104 | 209 | 891 | 1.19 |
| KCZ5 | 2.631 | 25.87 | 1.547 | 8.204 | 84 | 347 | 945 | 0.68 |
| NzZ0 | 2.559 | 24.41 | 1.507 | 7.268 | 91 | 254 | 794 | 0.25 |
| NzZ1 | 2.635 | 23.92 | 1.520 | 7.274 | 94 | 276 | 810 | 0.23 |
| NzZ3 | 2.704 | 23.94 | 1.535 | 7.448 | 81 | 251 | 837 | 0.14 |
| NzZ5 | 2.738 | 23.88 | 1.544 | 7.535 | 79 | 189 | 851 | 0.08 |
| NzZ7 | 2.830 | 23.53 | 1.564 | 7.651 | 80 | 172 | 862 | 0.04 |
| KzZ0 | 2.570 | 26.17 | 1.511 | 7.841 | 103 | 269 | 852 | 0.84 |
| KzZ1 | 2.613 | 26.03 | 1.518 | 7.886 | 98 | 262 | 888 | 0.63 |
| KzZ3 | 2.635 | 26.11 | 1.525 | 7.995 | 89 | 227 | 947 | 0.40 |
| KzZ5 | 2.737 | 25.89 | 1.545 | 8.190 | 86 | 249 | 978 | 0.36 |
| NKCZ1 | 2.505 | 25.15 | 1.519 | 7.636 | 106 | 345 | 835 | 0.52 |
| NKzZ1 | 2.600 | 25.20 | 1.516 | 7.605 | 95 | 282 | 827 | 0.13 |
| NCzZ1 | 2.558 | 24.12 | 1.518 | 7.312 | 74 | 291 | 801 | 0.26 |
| KCzZ1 | 2.536 | 26.43 | 1.515 | 7.970 | 88 | 236 | 863 | 0.65 |
| NKCzZ1 | 2.554 | 25.30 | 1.518 | 7.669 | 84 | 356 | 834 | 0.23 |
| NKCZ3 | 2.571 | 24.98 | 1.530 | 7.715 | 100 | 279 | 850 | 0.25 |
| NKzZ3 | 2.661 | 24.93 | 1.528 | 7.677 | 86 | 217 | 837 | 0.17 |
| NCzZ3 | 2.628 | 23.95 | 1.532 | 7.422 | 80 | 281 | 832 | 0.25 |
| KCzZ3 | 2.589 | 26.03 | 1.525 | 7.983 | 106 | 173 | 871 | 0.33 |
| NKCzZ3 | 2.620 | 24.83 | 1.532 | 7.692 | 98 | 274 | 834 | 0.12 |
| NKCZ5 | 2.655 | 24.64 | 1.548 | 7.829 | 97 | 269 | 883 | 0.21 |
| NKzZ5 | 2.777 | 24.59 | 1.548 | 7.805 | 85 | 216 | 871 | 0.10 |
| NCzZ5 | 2.750 | 23.56 | 1.556 | 7.574 | 91 | 269 | 855 | 0.18 |
| KCzZ5 | 2.690 | 25.64 | 1.545 | 8.111 | 84 | 246 | 946 | 0.29 |
| NKCzZ5 | 2.728 | 24.58 | 1.554 | 7.877 | 88 | 242 | 845 | 0.09 |
| NKCZ7 | 2.726 | 24.49 | 1.564 | 7.963 | 81 | 275 | 905 | 0.09 |
| NKzZ7 | 2.852 | 24.45 | 1.565 | 7.966 | 78 | 220 | 904 | 0.09 |
| NCzZ7 | 2.812 | 23.47 | 1.569 | 7.692 | 77 | 258 | 877 | 0.17 |
| KCzZ7 | 2.760 | 25.49 | 1.560 | 8.248 | 69 | 251 | 983 | 0.20 |
| NKCzZ7 | 2.797 | 24.40 | 1.564 | 7.942 | 77 | 238 | 875 | 0.10 |

and $ZrO_2$–$SiO_2$ mol fractions are tightly negatively correlated. Thus the $x_2$, $x_4$, and $x_6$ variables were skipped from the regression equation. Similarly also the $x_8 = x_2^2$, $x_{10} = x_4^2$, and $x_{12} = x_6^2$ variables were skipped. Finally the $x_7 = x_1^2$, $x_9 = x_3^2$, $x_{11} = x_5^2$, and $x_{15} = x_5x_6$ were deleted due to strong mutual correlations with retained independent variables. Thus after the correlation analysis the reduced regression function resulted:

$$p(\vec{x})\ a_0 + a(Na_2O)x(Na_2O) + a(CaO)x(CaO) + \\ + a(ZrO_2)x(ZrO_2) + a(Na_2O, K_2O)[x(Na_2O)x(K_2O)] \\ + a(CaO, ZnO)[x(CaO)\ x(ZnO)] \tag{6}$$

In the above equation only uncorrelated independent variables representing the interactions between mutually substituted oxides are considered. For the sake of completeness three other terms representing the interactions between the pairs of mutually substituted oxides, i.e. ($Na_2O$, $K_2O$) - (CaO, ZnO), (CaO, ZnO) - ($SiO_2$, $ZrO_2$), and ($Na_2O$, $K_2O$) - ($SiO_2$, $ZrO_2$), were added to the above regression function, giving the final form used for the multilinear regression analysis:

$$p(\vec{x})\ a_0 + a(Na_2O)x(Na_2O) + a(CaO)x(CaO) + \\ a(ZrO_2)x(ZrO_2) + a(Na_2O, K_2O)[x(Na_2O)x(K_2O)] + \\ + a(CaO, ZnO)[x(CaO)\ x(ZnO)] + \\ + a(Na_2O, ZrO_2)[x(Na_2O)x(ZrO_2)] + \\ + a(CaO, ZrO_2)[x(CaO)x(ZrO_2)] \tag{7}$$

Using the above regression equation the compositional dependences of all measured properties were analyzed. Based on the Student's $t$-statistics value only the statistically significant terms were retained in the Equation (7). The obtained results are summarized in Tables 4 and 5. Experimental and calculated values of

Table 3. Correlation coefficients between independent variables defined by the Equation (5). Statistically significant correlations are depicted by bold letters.

| | $\xi_1$ | $\xi_2$ | $\xi_3$ | $\xi_4$ | $\xi_5$ | $\xi_6$ | $\xi_7$ | $\xi_8$ | $\xi_9$ | $\xi_{10}$ | $\xi_{11}$ | $\xi_{12}$ | $\xi_{13}$ | $\xi_{14}$ | $\xi_{15}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\xi_1$ | 1.00 | -0.99 | 0.02 | 0.01 | 0.11 | -0.10 | 0.96 | -0.95 | 0.05 | 0.02 | 0.12 | -0.10 | -0.02 | -0.03 | 0.10 |
| $\xi_2$ | -0.99 | 1.00 | -0.03 | 0.01 | -0.11 | 0.08 | -0.95 | 0.96 | -0.06 | -0.00 | -0.12 | 0.07 | 0.03 | 0.03 | -0.11 |
| $\xi_3$ | 0.02 | -0.03 | 1.00 | -0.99 | 0.05 | 0.04 | 0.01 | -0.03 | 0.96 | -0.94 | 0.04 | 0.04 | -0.01 | 0.01 | 0.05 |
| $\xi_4$ | 0.01 | 0.01 | -0.99 | 1.00 | 0.05 | -0.16 | 0.02 | 0.00 | -0.94 | 0.96 | 0.05 | -0.16 | 0.02 | 0.03 | 0.04 |
| $\xi_5$ | 0.11 | -0.11 | 0.05 | 0.05 | 1.00 | -0.94 | 0.06 | -0.17 | 0.02 | 0.02 | 0.96 | -0.94 | 0.17 | 0.23 | 1.00 |
| $\xi_6$ | -0.10 | 0.08 | 0.04 | -0.16 | -0.94 | 1.00 | -0.08 | 0.12 | 0.05 | -0.14 | -0.91 | 1.00 | -0.18 | -0.24 | -0.93 |
| $\xi_7$ | 0.96 | -0.95 | 0.01 | 0.02 | 0.06 | -0.08 | 1.00 | -0.84 | 0.04 | 0.02 | 0.08 | -0.07 | -0.28 | -0.03 | 0.06 |
| $\xi_8$ | -0.95 | 0.96 | -0.03 | 0.00 | -0.17 | 0.12 | -0.84 | 1.00 | -0.04 | -0.00 | -0.17 | 0.12 | -0.24 | 0.00 | -0.17 |
| $\xi_9$ | 0.05 | -0.06 | 0.96 | -0.94 | 0.02 | 0.05 | 0.04 | -0.04 | 1.00 | -0.83 | 0.01 | 0.05 | -0.03 | -0.25 | 0.03 |
| $\xi_{10}$ | 0.02 | -0.00 | -0.94 | 0.96 | 0.02 | -0.14 | 0.02 | -0.00 | -0.83 | 1.00 | 0.02 | -0.14 | 0.04 | -0.23 | 0.02 |
| $\xi_{11}$ | 0.12 | -0.12 | 0.04 | 0.05 | 0.96 | -0.91 | 0.08 | -0.17 | 0.01 | 0.02 | 1.00 | -0.91 | 0.16 | 0.23 | 0.95 |
| $\xi_{12}$ | -0.10 | 0.07 | 0.04 | -0.16 | -0.94 | 1.00 | -0.07 | 0.12 | 0.05 | -0.14 | -0.91 | 1.00 | -0.18 | -0.24 | -0.93 |
| $\xi_{13}$ | -0.02 | 0.03 | -0.01 | 0.02 | 0.17 | -0.18 | -0.28 | -0.24 | -0.03 | 0.04 | 0.16 | -0.18 | 1.00 | 0.03 | 0.16 |
| $\xi_{14}$ | -0.03 | 0.03 | 0.01 | 0.03 | 0.23 | -0.24 | -0.03 | 0.00 | -0.25 | -0.23 | 0.23 | -0.24 | 0.03 | 1.00 | 0.23 |
| $\xi_{15}$ | 0.10 | -0.11 | 0.05 | 0.04 | 1.00 | -0.93 | 0.06 | -0.17 | 0.03 | 0.02 | 0.95 | -0.93 | 0.16 | 0.23 | 1.00 |

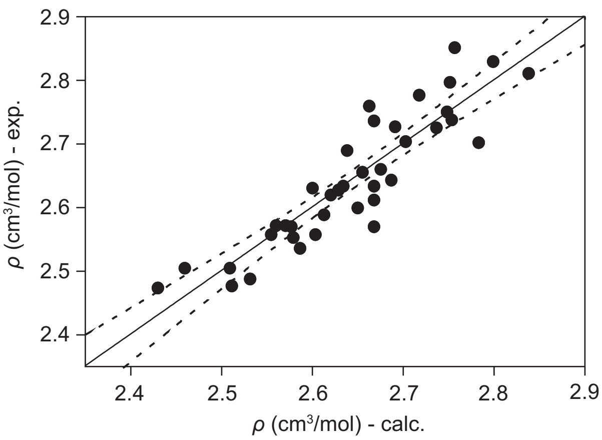


Figure 1. Comparison of experimental and calculated values of the glass density.

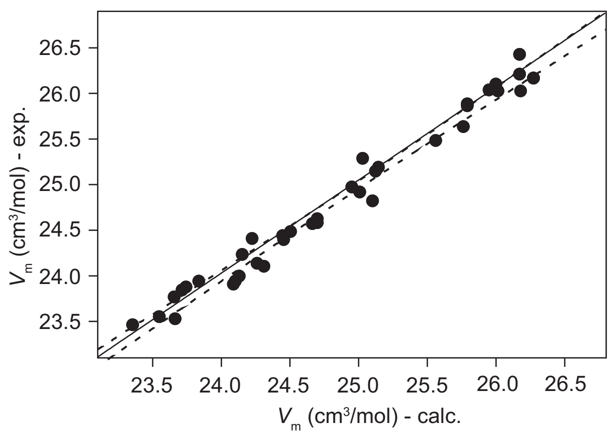


Figure 2. Comparison of experimental and calculated values of the molar volume.

studied properties are compared in Figures 1-8. It can be seen that, with the exception of thermal expansion coefficients, the correlation coefficients of obtained regression equations are higher than 0.9. Analogous behavior can be seen for the resulting standard deviations of approximations and Fisher's statistics. Best results were obtained for molar volume and molar refractivity where the quasi ideal behavior is observed (no interaction terms are present) and the standard deviations of approximations are close to the values of

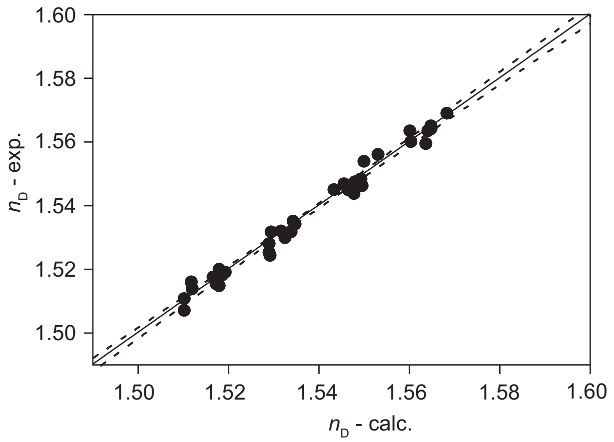


Figure 3. Comparison of experimental and calculated values of the refractive index.

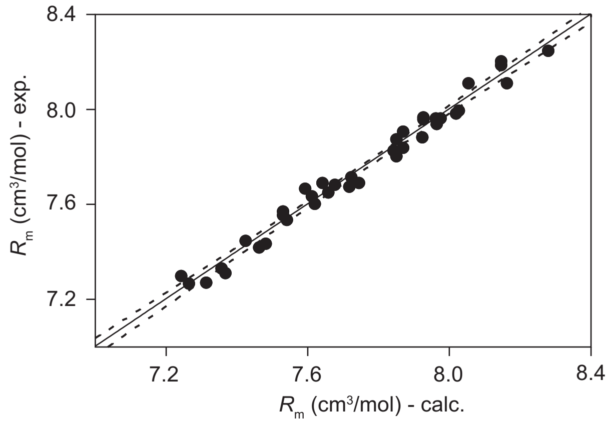


Figure 4. Comparison of experimental and calculated values of the molar refractivity.

Table 4. Results of multilinear regression analysis by the Equation (7), $s_{apr}$ - standard deviation of approximation, $r$ - correlation coefficient, $F$ - Fisher's F-statistics.

| Parameter | $\rho$□/ (g/cm$^3$) | $V_m$ (cm$^3$/mol) | $n_D$ | $R_m$ (cm$^3$/mol) |
|---|---|---|---|---|
| $a_0$ | 2.669 ± 0.016 | 26.27 ± 0.04 | 1.510 ± 0.001 | 7.868 ± 0.013 |
| $a(Na_2O)$ | -0.43 ± 0.19 | 13.87 ± 0.36 | – | -4.09 ± 0.11 |
| $a(CaO)$ | -1.86 ± 0.30 | | 0.020 ± 0.010 | – |
| $a(ZrO_2)$ | – | -9.87 ± 0.88 | 0.678 ± 0.022 | 5.65 ± 0.26 |
| $a(Na_2O, K_2O)$ | – | – | – | – |
| $a(CaO, ZnO)$ | – | – | – | – |
| $a(Na_2O, CaO)$ | – | – | – | – |
| $a(Na_2O, ZrO_2)$ | 20.8 ± 4.1 | – | 0.599 ± 0.163 | – |
| $a(CaO, ZrO_2)$ | 24.3 ± 6.7 | – | – | – |
| $s_{apr}$ | 0.047 | 0.132 | 0.002 | 0.039 |
| $r$ | 0.901 | 0.990 | 0.992 | 0.991 |
| $F$ | 36 | 879 | 723 | 909 |

Table 5. Results of multilinear regression analysis by the Equation (7), $s_{apr}$ - standard deviation of approximation, $r$ - correlation coefficient, $F$ - Fisher's F-statistics.

| Parameter | $10^7 \times a_g$ (K$^{-1}$) | $10^7 \times a_m$ (K$^{-1}$) | $T_g$ (K) | $CD$ (ml) |
|---|---|---|---|---|
| $a_0$ | 102 ± 3 | 274 ± 11 | 874 ± 8 | 0.66 ± 0.08 |
| $a(Na_2O)$ | -91 ± 27 | – | -514 ± 75 | -3.26 ± 0.76 |
| $a(CaO)$ | 72 ± 25 | – | -226 ± 99 | 6.89 ± 1.31 |
| $a(ZrO_2)$ | -350 ± 72 | -784 ± 244 | 1769 ± 167 | -6.98 ± 2.05 |
| $a(Na_2O, K_2O)$ | – | – | -5132 ± 910 | -37.02 ± 8.87 |
| $a(CaO, ZnO)$ | -1927 ± 856 | – | -5921 ± 1969 | -44.73 ± 19.13 |
| $a(Na_2O, CaO)$ | – | 4820 ± 1196 | 3096 ± 958 | -24.20 ± 1.00 |
| $a(Na_2O, ZrO_2)$ | 1617 ± 688 | – | -4778 ± 1592 | 51.57 ± 17.16 |
| $a(CaO, ZrO_2)$ | – | – | – | -55.07 ± 25.53 |
| $s_{apr}$ | 6 | 37 | 14 | 0.14 |
| $r$ | 0.807 | 0.643 | 0.961 | 0.918 |
| $F$ | 12 | 12 | 52 | 18 |

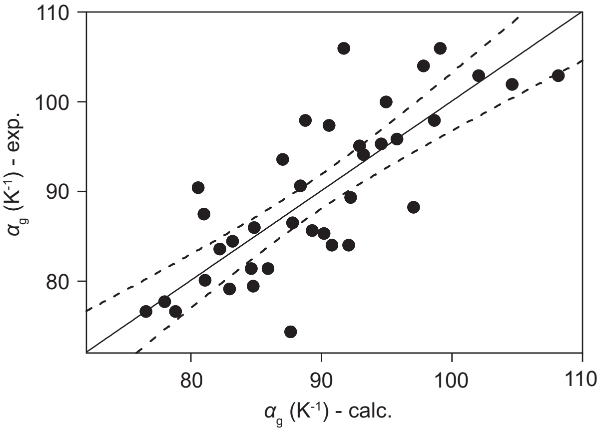


Figure 5. Comparison of experimental and calculated values of glass thermal expansion coefficient.

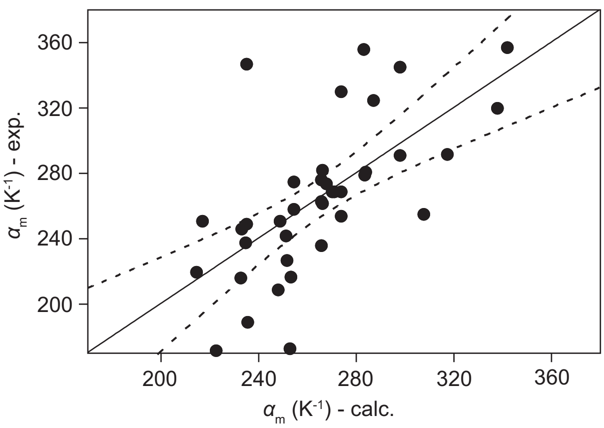


Figure 6. Comparison of experimental and calculated values of metastable melt thermal expansion coefficient.

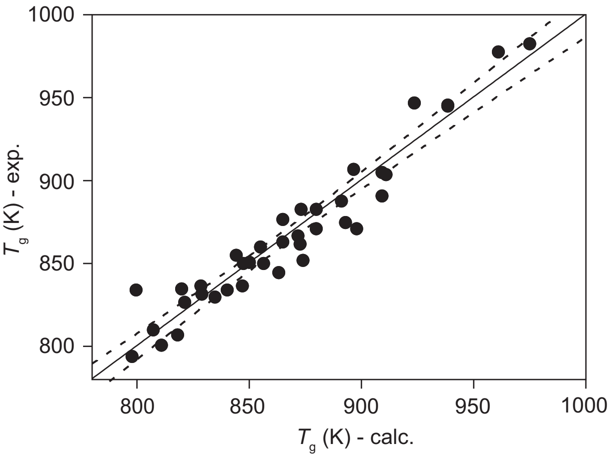


Figure 7. Comparison of experimental and calculated values of the glass transition temperature.

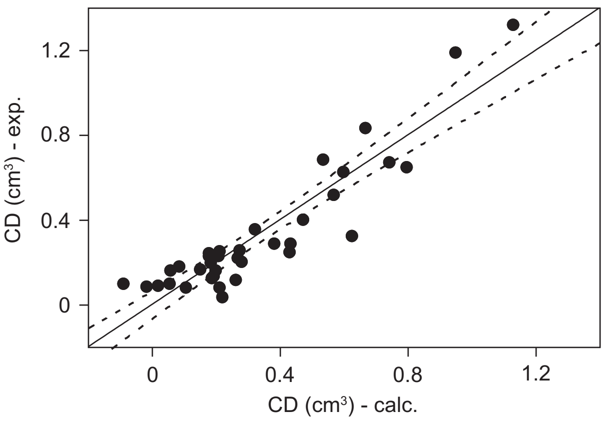


Figure 8. Comparison of experimental and calculated values of the chemical durability.

the experimental error. Similar situation is found for the refractive index, but the interaction between $Na_2O$ and $ZrO_2$ is statistically significant in this case. On the other side, the most pronounced non-linearity was observed in case of the chemical durability and glass transition temperature. It can be accepted because there is no physical reason for linear behavior of these complex quantities. In similar position are the thermal expansion coefficients, where various mutual interactions were detected. In case of thermal expansion of metastable melt, $a_m$, the regression equation is practically useless (see Figure 6). Generally speaking the composition-property study based on more appropriate compositional model, i.e. the thermodynamic model, is needed.

## CONCLUSIONS

It can be concluded that the observed property-composition dependencies are in qualitative agreement with the results obtained for glasses with lower zirconia content in our previous work [1-3]. The $K_2O$ / $Na_2O$ substitution increases the value of molar volume, molar refractivity, and *CD*, and decreases the value of refractivity index, and melt density. The ZnO / CaO substitution lightly decreases the value of molar volume, refractivity index, molar refractivity, and *CD*. The $ZrO_2$ / $SiO_2$ substitution increases the value of refractivity index, and molar refractivity, and decreases the value of molar volume, and *CD*.

The results of the multilinear regression analysis pointed out the ideal behavior of molar volume and molar refractivity. The strongest influence of mutual oxide interactions was found for chemical durability and glass transition temperature. The regression analysis of compositional dependence of metastable melt thermal expansion coefficient practically failed. The need of property-composition study based on the thermodynamic model was pointed out.

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