PROPERTIES OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES III.

RADOVAN KARELL, MÁRIA CHROMČÍKOVÁ, MAREK LIŠKA

Vitrum Laugaricio - Joint Glass Centre of the Institute of Inorganic Chemistry,
Slovak Academy of Sciences, Alexander Dubček University of Trenčín
and RONA, a.s., Študentská 2, Trenčín, SK- 911 50, Slovak Republic,

E-mail: karell@tnuni.sk

Viscosity, density, glass transition temperature, T_g, refractive index, n_D, molar refractivity, R_m, and chemical durability, CD, of $xNa_2O\cdot(15-x)K_2O\cdot yCaO\cdot(10-y)ZnO\cdot zZrO_2\cdot(75-z)SiO_2$ ($x = 0$, 7.5, 15; $y = 0$, 5, 10; $z = 1$, 3) glasses were measured. The temperature dependence of viscosity was described by Andrade's equation and the temperature independent values of the viscous flow activation energy, E_η, were calculated. The effect of K_2O/Na_2O, ZnO/CaO, and ZrO_2/SiO_2 substitution on the values of V_m, n_D, R_m, T_g, E_η, and CD was quantified by multilinear regression analysis. It was statistically confirmed that the K_2O/Na_2O substitution increases the value of V_m, R_m, T_g, E_η, and CD and decreases the value of n_D. The ZnO/CaO substitution increases the value of T_g, and decreases the value of V_m, n_D, R_m, E_η, and CD. The ZrO_2/SiO_2 substitution increases the value of n_D, R_m, T_g, and E_η, and decreases the value of V_m, and CD.

INTRODUCTION

Silicate glasses containing zirconia play a significant role both in the igneous petrology [1] and glass technology [2]. Due to the non-toxicity and extremely high chemical durability in alkaline conditions these glasses are used for the production of alkali-resistant fibers for Portland cement composites [3]. Both the thermal expansion coefficient and the glass transition temperature are positively correlated with the ZrO_2 content in silicate glass [4-6]. In addition to the chemical durability the high density and high value of refractive index and dispersion predetermined these glasses for production of ecologically friendly barium- and lead-free crystal glass [7, 8]. In addition to ZrO_2, other oxides of elements as CaO, ZnO, and TiO_2 are used to substitute harmful lead- and barium-oxide. On the other side, zirconia increases the viscosity of the glass melt [9] and the melting of the glass batch containing zirconium-containing raw materials (typically zircon) needs increased temperature and longer time. Thus, the corrosion of the refractory materials is more pronounced [2, 10].

EXAFS studies of Zr coordination in selected silicate glasses have shown that variations in the local environment of Zr are relatively small [11]. In silicate glasses with lower ZrO_2 concentrations (1-4 wt.%) Farges and Calas [12] found Zr to be mainly 6 coordinated. The abundance of 6 coordinated Zr should increase with melt depolymerization as a result of the increasing network modifier content. With respect to the main coordination number, zirconia can be classified as network-modifying oxide according to the Zachariasens' rules. However its structural position strengthens the silicate network via forming the covalent Zr–O–Si bridges. Thus its influence on concentration dependence of various physical and chemical properties resembles the network-forming oxides. Therefore the literature information about the network-forming/modifying character of ZrO_2 is relatively contradictory. For example, Ringwood [13] stated that ZrO_2 is a network-former producing tetrahedral ZrO_4 groups. Furthermore, Linthout [14] inferred that ZrO_2 is a network modifier rather a network former based on crystal-chemical reasoning.

The possible structural model of 6-coordinated zirconium in silicate glasses suggested by Farges [11] on the basis of the EXAFS study consists in ZrO_6 octahedron with four bridging and two non-bridging oxygen atoms (schematically $[ZrO_2O_{4/2}]^{4-}$). Thus, ZrO_2 not only takes part in the formation of the silicate network, but in addition it heals the broken Si–O–Si bridges according to the reaction:

$$4 \equiv Si–O^- + ZrO_2 \rightarrow 2 \equiv Si–O–Si \equiv + [ZrO_2O_{4/2}]^{4-} \quad (1)$$
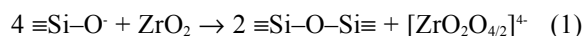
Characterization of the Zn environments in silicate glasses was done using XAS and X-ray scattering techniques [15]. The tetrahedral ZnO_4 coordination is preferred in alkali silicate glasses, i.e. the zinc oxide acts as networkformer. As in case of ZrO_2 the network forming position of ZnO decreases the effective modifier concentration due to the reaction:

$$2 \equiv Si–O^- + ZnO \rightarrow \equiv Si–O–Si \equiv + [ZnO_{4/2}]^{2-} \quad (2)$$
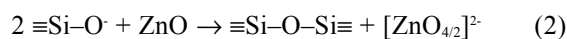
During the development of zirconia containing silicate glasses with targeted properties the multi-component, i.e. more than three-component, zirconia containing silicate systems are commonly studied [17-20]. However, the study of simpler model systems is needed to envisage the structure-property relationships with respect to the structural position of ZrO_2 in the silicate glass and melt. Moreover, the thermodynamic models based on the regular solution theory can be simply constructed for simple oxide systems to verify the structural assumptions proposed on the basis of experimentally determined composition-property relationships [21]. The literature data concerning the composition - property relationships for more than three component zirconia containing silicate systems are relatively scarce [22, 23]. Therefore the effect of the equimolar ZrO_2/SiO_2 substitution in sodium- and potassium- trisilicate glasses $15M_2O \cdot 10CaO \cdot xZrO_2 \cdot (75-x)SiO_2$ and $15M_2O \cdot 10ZnO \cdot xZrO_2 \cdot (75-x)SiO_2$ (M = Na, K, x = 1, 3, 5, and 7) was studied in our previous works [24,25]. The present paper deals with the equimolar K_2O/Na_2O, ZnO/CaO, and ZrO_2/SiO_2 substitution in glasses with the trisilicate stoichiometry $xNa_2O \cdot (15-x)K_2O \cdot yCaO \cdot (10-y)ZnO \cdot zZrO_2 \cdot (75-z)SiO_2$ (x = 0, 7.5, 15; y = 0, 5, 10; z = 1, 3).

EXPERIMENTAL

The glass batches were prepared by mixing of powdered Na_2CO_3 (AFT, p.a.), K_2CO_3 (Fluka, p.a.), ZnO (Fluka, p.a.), $ZrSiO_4$ (Aldrich, p.a.) and 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. Theoretical composition and abbreviation of glass samples is summarized in Table 1.

Table 1. The composition and abbreviation of studied glasses.

Glass	Na_2O	K_2O	CaO	ZnO	ZrO_2	SiO_2
NKCZ1	7.5	7.5	10	-	1	74
NKzZ1	7.5	7.5	-	10	1	74
NCzZ1	15	-	5	5	1	74
KCzZ1	-	15	5	5	1	74
NKCzZ1	7.5	7.5	5	5	1	74
NKCZ3	7.5	7.5	10	-	3	72
NKzZ3	7.5	7.5	-	10	3	72
NCzZ3	15	-	5	5	3	72
KCzZ3	-	15	5	5	3	72
NKCzZ3	7.5	7.5	5	5	3	72

Glass transition temperature, T_g, were obtained by thermodilatometry (Netzsch, TMA 402 and TA Q400EM) during cooling from sufficiently high temperature by the cooling rate of 5°C/min. The densities of glasses at laboratory temperature were measured by Archimedes method by dual weighting in air and in distilled water. Refractive index 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 [26] at 98°C.

The low-temperature viscosities between 10^8 and 10^{12} dPa.s were measured by thermo-mechanical analyzer (Netzsch, TMA 402). The viscosity value, η, was calculated from the measured deformation rate $d\varepsilon/dt$ and the known value of axial load G on orthorhombic (approx. 5 mm × 5 mm × 20 mm) sample with cross-section S:

$$\eta = \frac{G}{3S(d\varepsilon/dt)} \qquad (3)$$

RESULTS AND DISCUSSION

The measured values of density, glass transition temperature, refractivity index, and chemical durability against water (CD, expressed in cm³ of 10^{-2} molar HCl [26]) are summarized in Table 2 together with the molar refractivity calculated by:

$$R_m = \frac{\left(n_D^{20}\right)^2 - 1}{\left(n_D^{20}\right)^2 + 2} \frac{M_g}{\rho} \qquad (4)$$

where M_g is the molar (formula) weight of glass, n_D^{20} is the refractive index and ρ is the glass density.

For comparison, the results obtained in our previous works [24, 25] for the $15M_2O \cdot 10RO \cdot xZrO_2 \cdot (75-x)SiO_2$ (M = Na, K; R = Ca, Zn; x = 1, 3) glasses are also reported in the Table 2. As expected, the chemical durability steeply increases (i.e. CD value decreases) with increasing ZrO_2 content. On the other hand, the chemical durability is significantly lower for the potassium glasses, namely for low ZrO_2 content, in comparison with the corresponding sodium ones. It can be also deduced that increasing ZnO content leads to increase of chemical durability.

The density, glass transition temperature, refractive index and molar refractivity values are positively correlated with ZrO_2 content. The increase of T_g with increasing ZrO_2 content in silicate glasses was also reported by Takahashi [5], and Fisher [6].

The temperature dependence of low temperature viscosity was described by the Arrhenius-like equation (also known as Andrade's equation):

$$\log(\eta/\text{dPa.s}) = A + B/T \qquad (5)$$

where A, and B are constants routinely determined by the regression analysis, and T is thermodynamic temperature (Table 3). The temperature independent viscous flow activation energy, E_a, was calculated by:

$$E_a = [\partial \ln \eta / \partial (1/T)]_P = \ln(10)RB = 2.303RB \qquad (6)$$

where R is the molar gas constant. Table 3 summarizes the values of A, and B coefficients (Equation (5)), and the values of activation energy calculated according the Equation (6).
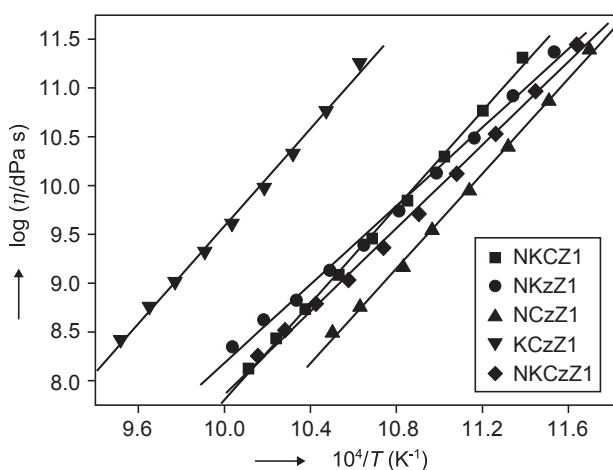
Experimental values of viscosity are plotted in $\log(\eta/\text{dPa.s})$ versus 10^4 K/T coordinate system in Figure 1 for Z1 glasses (i.e. glasses containing 1 mole % of ZrO_2), and in Figure 2 for Z3 glasses. In both plotted series the highest viscosity values are observed for the sodium free glasses. Moreover, the steepest linear dependence (i.e. the highest viscous flow activation energy) is found for the glasses containing 10 mole % of CaO.

In the present study the glass compositions are derived from three equimolar substitutions, e.g. K_2O/Na_2O, ZnO/CaO, and ZrO_2/SiO_2. In such situation some trends are not straightforwardly identified nor from the tabular form of the measured data nor from the graphical data presentation. Moreover, in some cases it is hard to identify whether the visually identified trends

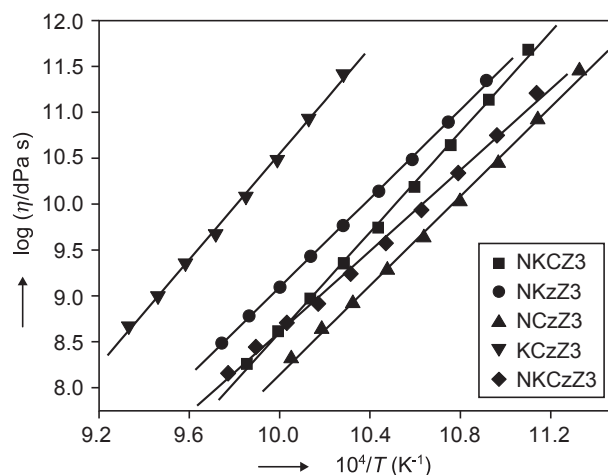Figure 1. Arrhenius plot of viscosity - temperature dependence for Z1 glasses.

Figure 2. Arrhenius plot of viscosity - temperature dependence for Z3 glasses.

Table 2. Measured physical and chemical properties of studied glasses. The values for analogous lime glasses NCZ*n*, NzZ*n*, KCZ*n* and KzZ*n* (taken from [24,25]) are reported for comparison.

Glass	V_m (cm³/mol)	ρ (g/cm³)	T_g (K)	n_D^{20}	R_m (cm³/mol)	CD (cm³)
NKCZ1	25.16	2.505 ± 0.001	835	1.5193	7.64	0.52 ± 0.01
NKzZ1	25.21	2.600 ± 0.001	827	1.5155	7.64	0.13 ± 0.02
NCzZ1	24.18	2.558 ± 0.001	801	1.5184	7.33	0.26 ± 0.03
KCzZ1	26.30	2.536 ± 0.001	863	1.5149	7.93	0.65 ± 0.1
NKCzZ1	25.17	2.554 ± 0.001	834	1.5183	7.63	0.23 ± 0.01
NCZ1	24.22	2.506 ± 0.001	830	1.5193	7.35	0.69 ± 0.03
NzZ1	23.96	2.635 ± 0.002	810	1.5202	7.29	0.23 ± 0.01
KCZ1	26.32	2.489 ± 0.001	883	1.5191	7.99	1.33 ± 0.01
KzZ1	26.01	2.613 ± 0.001	888	1.5178	7.88	0.63 ± 0.04
NKCZ3	25.00	2.571 ± 0.001	850	1.5300	7.72	0.25 ± 0.04
NKzZ3	25.11	2.661 ± 0.001	837	1.5281	7.73	0.17 ± 0.01
NCzZ3	24.02	2.628 ± 0.001	832	1.5321	7.44	0.25 ± 0.04
KCzZ3	26.25	2.589 ± 0.001	871	1.5254	8.04	0.33 ± 0.03
NKCzZ3	25.05	2.620 ± 0.001	834	1.5318	7.75	0.12 ± 0.01
NCZ3	24.16	2.572 ± 0.001	850	1.5319	7.49	0.29 ± 0.01
NzZ3	23.81	2.704 ± 0.007	837	1.5345	7.41	0.14 ± 0.01
KCZ3	26.03	2.573 ± 0.001	895	1.5352	8.11	1.19 ± 0.01
KzZ3	26.27	2.635 ± 0.001	947	1.5245	8.04	0.40 ± 0.01

are statistically significant. Thus the multilinear regression analysis has to be used for statistically substantiated identification of various compositional trends. Generally the value of any measured physical quantity can be considered as a linear (or quadratic) function of independent variables defined as molar fractions (or mole %) of individual oxides. This approach is formally approved - at least - by the Fourier deconvolution truncated after the linear (quadratic) terms. However, only linearly independent terms can be used in the regression analysis. In the case of the present study the three linear bonds between mole % of individual oxides are present:

$$x(K_2O) = 15 - x(Na_2O) \qquad (7)$$

$$x(ZnO) = 10 - x(CaO) \qquad (8)$$

$$x(ZrO_2) = 75 - x(SiO_2) \qquad (9)$$

Then the general form of the polynomial function containing the interaction terms between mutually substituted oxides (e.g. $Na_2O–K_2O$, $CaO–ZnO$, and $ZrO_2–SiO_2$) simplifies to the quadratic equation in only three independent variables (e.g. $x(Na_2O)$, $x(CaO)$, and $x(ZrO_2)$):

$$
\begin{aligned}
p(\vec{x}) =\ & [a(Na_2O) - a(K_2O) + 15a(Na_2O,K_2O)]x(Na_2O) + \\
& + [a(CaO) - a(ZnO) + 10a(CaO,ZnO)]x(CaO) + \\
& + [a(ZrO_2) - a(SiO_2) + 75a(ZrO_2,SiO_2)]x(ZrO_2) + \\
& + 15a(K_2O) + 10a(ZnO) + 75a(SiO_2) - \\
& - a(Na_2O,K_2O)x^2(Na_2O) - a(CaO,ZnO)x^2(CaO) - \\
& - a(ZrO_2,SiO_2)]x^2(ZrO_2)
\end{aligned}
$$

$$(10)$$

and

$$
\begin{aligned}
p(\vec{x}) =\ & q_0 + q(Na_2O)x(Na_2O) + q(CaO)x(CaO) + \\
& + q(ZrO_2)x(ZrO_2) - a(Na_2O,K_2O)x^2(Na_2O) \\
& - a(CaO,ZnO)x^2(CaO) - a(ZrO_2,SiO_2)]x^2(ZrO_2)
\end{aligned}
$$

$$(11)$$

where

$$q_0 = 15a(K_2O) + 10a(ZnO) + 75a(SiO_2) \qquad (12)$$

$$q(Na_2O) = a(Na_2O) - a(K_2O) + 15a(Na_2O, K_2O) \quad (13)$$

$$q(CaO) = a(CaO) - a(ZnO) + 10a(CaO, ZnO) \quad (14)$$

$$q(ZrO_2) = a(ZrO_2) - a(SiO_2) + 75a(ZrO_2, SiO_2) \quad (15)$$

Using the Equation (11) the regression analysis of the experimental data from Table 2 was performed. The obtained results are summarized in Table 4 together with some statistical characteristics. The calculated and experimental values are compared in Figure 3. Only the statistically significant terms based on the Student's t-statistics on the 95 % significant level were retained in the equations in most cases. However in the case of refractivity index the less robust estimates were obtained and the $q(CaO)$ was retained at significance level of 83 %. Similarly for the molar volume the $q(CaO)$ value was accepted at significance level of 78 % and the $q(ZrO_2)$ value at significance level of 88 %. Thus the discussion of the impact of ZnO/CaO substitution on the refractivity index and the ZnO/CaO and ZrO_2/SiO_2 substitution on the molar volume are less statistically substantiated.

Table 3. Measured physical and chemical properties of studied glasses. The values for analogous lime glasses NCZ*n*, NzZ*n*, KCZ*n* and KzZ*n* (taken from [24,25]) are reported for comparison.

Glass	*A*	*B*	E_a (kJ/mol)	s_{apr} [log(η/dPas)]
NKCZ1	-16.88 ± 0.44	24679 ± 412	472 ± 8	0.051
NKzZ1	-11.93 ± 0.54	20113 ± 480	385 ± 10	0.075
NCzZ1	-17.12 ± 0.46	24320 ± 418	466 ± 8	0.046
KCzZ1	-15.38 ± 0.57	24969 ± 566	478 ± 11	0.061
NKCzZ1	-13.47 ± 0.46	21330 ± 426	408 ± 8	0.064
NCZ1	-17.97 ± 0.76	25526 ± 700	489 ± 13	0.087
NzZ1	-14.68 ± 0.50	22278 ± 453	426 ± 9	0.070
KCZ1	-20.26 ± 0.41	29769 ± 401	570 ± 8	0.034
KzZ1	-14.27 ± 0.73	24190 ± 736	463 ± 14	0.092
NKCZ3	-18.67 ± 0.38	27270 ± 363	522 ± 7	0.044
NKzZ3	15.05 ± 0,18	24147 ± 179	462 ± 3	0.020
NCzZ3	-16.13 ± 0.47	24273 ± 442	465 ± 8	0.076
KCzZ3	-18.27 ± 0.48	28821 ± 493	552 ± 9	0.043
NKCzZ3	-13.43 ± 0.49	22036 ± 468	422 ± 9	0.065
NCZ3	-18.26 ± 0.29	26658 ± 279	510 ± 5	0.032
NzZ3	-15.52 ± 0.34	24084 ± 328	461 ± 6	0.038
KCZ3	-22.68 ± 0.57	33018 ± 577	632 ± 11	0.028
KzZ3	-18.80 ± 0.59	30261 ± 617	579 ± 12	0.033

Table 4. Results of multi-linear regression analysis (see Equations 11-15), $s(p)$ - standard deviation of parameter p, s_{apr} - standard deviation of approximation, R - correlation coefficient, F - Fisher's F-statistics.

	V_m (cm³/mol)	n_D^{20}	R_m (cm³/mol)	T_g (K)	E_η (kJ/mol)	CD (cm³)
q_0	26.24	1.5090	7.844	867.4	461	0.74
$s(q_0)$	0.08	0.0017	0.014	6.4	20	0.11
$q(Na_2O)$	-0.1425	0.00021	-0.0409	-8.40	-21.7	-0.109
$s[q(Na_2O)]$	0.0045	0.00010	0.0008	1.25	4.1	0.023
$q(CaO)$	0.0087[n]	0.00022[n]	0.0058	-4.40	7.0	-
$s[q(CaO)]$	0.0068	0.00015	0.0013	1.88	1.7	-
$q(ZrO_2)$	-0.0458[n]	0.00625	0.0606	6.83	24.9	-0.084
$s[q(ZrO_2)]$	0.0276	0.00061	0.0051	2.12	6.9	0.038
$a(Na_2O, K_2O)$	-	-	-	0.3169	1.110	0.0053
$s[a(Na_2O, K_2O)]$	-	-	-	0.0785	0.262	0.0015
$a(CaO, ZnO)$	-	-	-	0.5331	-	0.0045
$s[a(CaO, ZnO)]$	-	-	-	0.1765	-	0.0009
F	335	37	850	28	17	16
R	0.993	0.942	0.997	0.963	0.916	0.913
s_{apr}	0.12	0.0026	0.022	8.6	29	0.16

[n] -statistically non-significant value at the 95-% confidence level - see text.

It can be seen (Table 4), that for the glass transition temperature, viscous flow activation energy, and chemical durability the simple additive scheme was insufficient and the Na_2O–K_2O interaction term was statistically significant for all these quantities. Moreover for T_g and CD the CaO–ZnO interaction term was statistically significant.

The results presented in Table 4 can be summarized in the following way:

The K_2O/Na_2O substitution:
- increases the value of: molar volume, molar refractivity, glass transition temperature, viscous flow activation energy, and CD;
- decreases the value of: refractivity index;
- the Na_2O–K_2O interaction amplifies the above effect of K_2O/Na_2O substitution for T_g, E, and CD.

The ZnO/CaO substitution:
- increases the value of: glass transition temperature;
- decreases the value of: molar volume, refractivity index, molar refractivity, viscous flow activation energy, and CD;
- the CaO–ZnO interaction amplifies the above effect of ZnO/CaO substitution for the glass transition temperature.

The ZrO_2/SiO_2 substitution:
- increases the value of: refractivity index, molar refractivity, glass transition temperature, and viscous flow activation energy;
- decreases the value of molar volume, and CD.

However the above conclusions are only qualitative as they are deduced only from the signs of the particular coefficients. The quantitative results can be obtained by taking the partial derivative of the particular equation with respect to the mole % of particular oxide. These values are constant, i.e. composition independent, for the equations without interaction terms.

CONCLUSION

The compositional dependence of measured physical properties of xNa$_2$O·(15-x)K$_2$O·yCaO·(10-y)ZnO·zZrO$_2$·(75-z)SiO$_2$ (x =0, 7.5, 15; y = 0, 5, 10; z = 1, 3) glasses was rationalized in terms of K_2O/Na_2O, ZnO/CaO, and ZrO_2/SiO_2 equimolar substitutions using the multilinear regression model containing the quadratic Na_2O–K_2O, CaO–ZnO, and ZrO_2–SiO_2 interaction terms. Regression treatment led to simple additive compositional schemes for molar volume, refractivity index, and molar refraction. The statistically significant Na_2O–K_2O interaction term was found for viscous flow activation energy, glass transition temperature, and chemical durability. For the last two quantities also the significance of CaO–ZnO interaction term was statistically proved. It was statistically confirmed that the K_2O/Na_2O substitution increases the value of V_m, R_m, T_g, E_η, and CD and decreases the value of n_D. The ZnO/CaO substitution increases the value of T_g and decreases the value of V_m, n_D, R_m, E_η, and CD. The ZrO_2/SiO_2 substitution increases the value of n_D, R_m, T_g, and E_η and decreases the value of V_m, and CD.
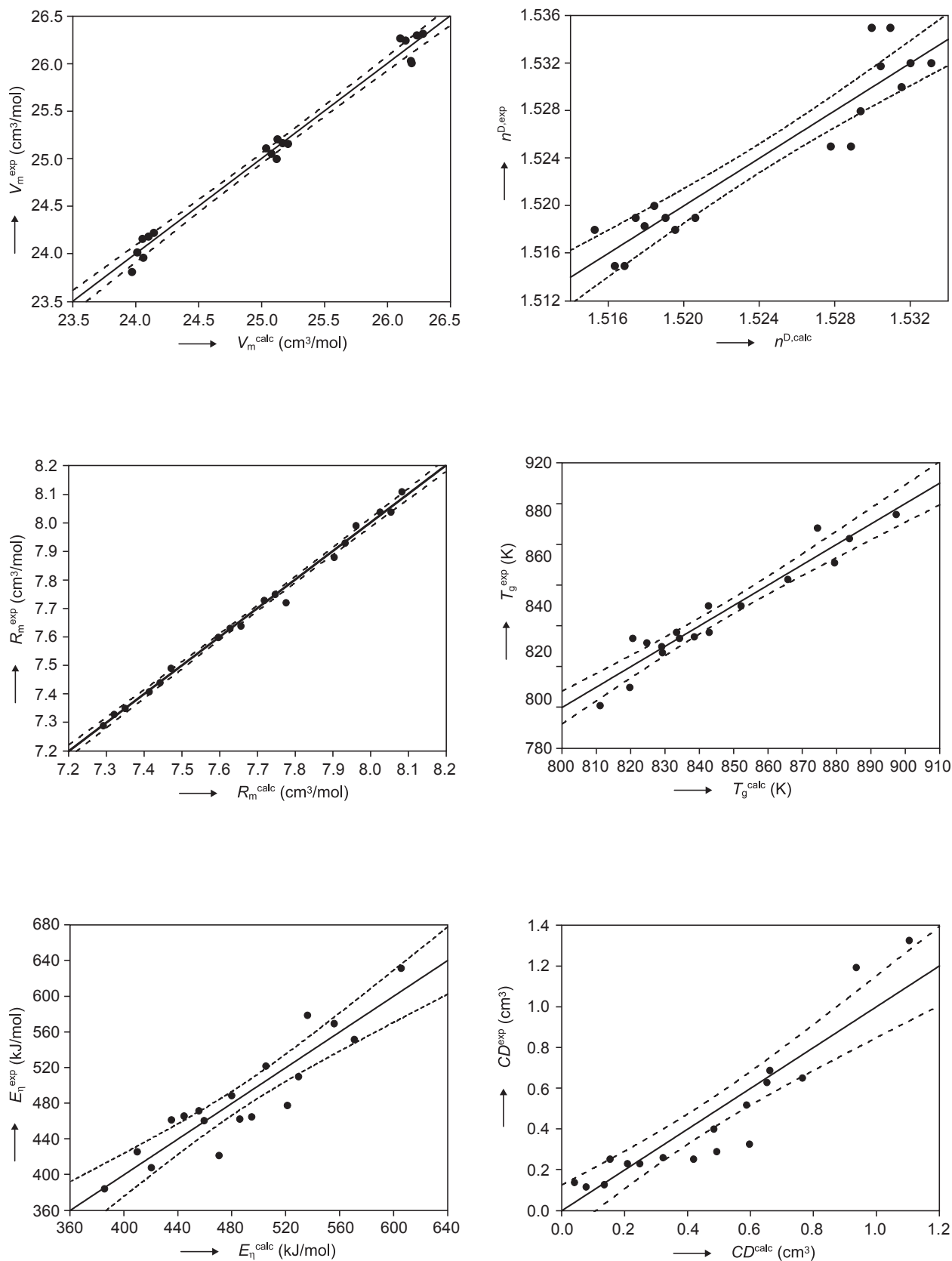
Figure 3. Comparison of experimental (exp) and calculated (calc) values of V_m, n_D, R_m, T_g, E_η, and CD. The dotted line corresponds to 95 % confidence limits.

Acknowledgement

References

1. Hofmann A.W.: Earth Planet Sci. Lett. *90*, 297 (1988).
2. Vogel W.: *Glass Chemistry*, Springer, Berlin 1994.
3. Proctor B. A., Yale B.: Phil.Trans.R.Soc.London *A 294*, 427 (1980).
4. Kheifets V. S., Shevyakov A. M., Tarlakov Yu. P., in: *Mekhanicheskije i teplovye svojstva i strojenie stekla*, pp. 280-285, Moscow 1972. (in Russian)
5. Takahashi K., Mochida N., Yoshida Y.: J.Ceram.Soc.Jpn. *85*, 330 (1977).
6. Fisher J. G., James P. F., Parker J. M.: J. Non - Cryst. Solids *351*, 623 (2005).
7. EU patent No. 91121730.5, 1991.
8. Czech patent No. WO 95/13993.
9. Volf M.B.: *Chemie skla*, SNTL, Praha 1971. (in Czech)
10. Hrma P.: Ceramics-Silikáty *50*, 57 (2006).
11. Ponader C. W., Brown Jr. G. E.: Geochim. Cosmochim. Acta, *55*, 1563 (1991).
12. Farges F., Calas G.: Amer. Mineral. *76*, 60 (1991).
13. Ringwood A. E.: Geochim.Cosmochim. Acta *7*, 189 (1955); *7*, 242 (1955).
14. Linthout K.: Contrib.Mineral.Petrol. *86*, 155 (1984).
15. McKeown D. A., Muller I. S., Buechele A. C., Pegg I. L.: J.Non-Cryst.Solids *261*, 155 (2000).
16. Calas G., Cormier L., Galoisy L., Jollivet P.: C. R. Chemie *5*, 831 (2002).
17. Liška M., Šimurka P.: Phys.Chem.Glasses *36*, 6, (1995).
18. Liška M., Hulínová H., Šimurka P., Antalík J.: Ceramics-Silikáty *39*, 20 (1995).
19. Šimurka P., Liška M., Antalík J.: Ceramics-Silikáty *39*, 9 (1995).
20. Chromčíková M., Liška M., Karell R, Martiš V.: Chem. Listy *98*, 584 (2004).
21. Liška M., Klement R., Macháček J., Gedeon O.: Phys. Chem. Glasses *46*, 108 (2005).
22. INTERGLAD, Ver. 6., http://www5.ngf.dion.ne.jp (2005).
23. SciGlass-6.5, http://www.scienceserve.com/Software/SciGlass (2005).
24. Karell R., Kraxner J., Chromčíková M.: Ceramics-Silikáty *50*, 78 (2006).
25. Karell R., Kraxner J., Chromčíková M., Liška M.: Ceramics-Silikáty *51*, 125 (2007).
26. ČSN ISO 70 0531.

VLASTNOSTI VYBRANÝCH
ZIRKONIČITANOVÝCH SKIEL III.

RADOVAN KARELL, MÁRIA CHROMČÍKOVÁ,
MAREK LIŠKA

*Vitrum Laugaricio - Centrum kompetencie skla
Ústavu anorganickej chémie SAV,
Trenčianskej univerzity A. Dubčeka a RONA, a.s.,
Študentská 2, 911 50 Trenčín, Slovenská republika*

U skiel zloženia xNa$_2$O·(15-x)K$_2$O·yCaO·(10-$_y$)ZnO·zZrO$_2$·(75-z)SiO$_2$ (x = 0, 7,5, 15; y = 0, 5, 10; z = 1, 3) bola zmeraná viskozita, hustota, teplota skleného prechodu, T_g, index lomu n_D a chemická odolnosť CD. Závislosť viskozity od reciprokej termodynamickej teploty sa určila pomocou Andradeho rovnice a tiež sa vypočítali hodnoty teplotne nezávislej aktivačnej energie viskózneho toku, E_η molárnej refrakcie, R_m, a molárneho objemu, V_m. Multilineárnou regresnou analýzou sa určil vplyv substitúcií K$_2$O/Na$_2$O, ZnO/CaO a ZrO$_2$/SiO$_2$. Štatisticky sa potvrdilo, že substitúcia K$_2$O/Na$_2$O spôsobuje nárast hodnôt V_m, R_m, T_g, E_η a CD, pokles hodnoty n_D; substitúcia ZnO/CaO zvyšuje T_g a znižuje hodnoty V_m, n_D, R_m, E_η a CD. Substitúcia ZrO$_2$/SiO$_2$ zvyšuje hodnoty n_D, R_m, T_g a E_η a spôsobuje pokles hodnôt V_m a CD.