

PROPERTIES OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES

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Viscosity, density, thermal expansion, glass transition temperature, refractive index, molar refraction, and chemical durability of $15M_2O \cdot 10CaO \cdot xZrO_2 \cdot (75-x)SiO_2$ ($M = Na$ for NCZ glasses, and $M = K$ for KCZ glasses; $x = 1, 3, 5,$ and 7) glasses were measured. The effect of SiO_2/ZrO_2 equimolar substitution on measured physical and chemical properties was discussed. Increasing content of ZrO_2 significantly improves the chemical durability against water in both studied glass series. The ZrO_2/SiO_2 substitution strengthens the silicate network and therefore increases the values of glass transition temperature, and viscosity and decreases the value of the thermal expansion coefficient. Molar refractivity depends linearly on the ZrO_2 content. The slope of the regression line is the same for both studied glass series, whereas the higher intercept for potassium glasses reflects the greater polarizability of the potassium cation with respect to the Na^+ cation. In comparison with the NCZ glasses both the viscosity and the viscous flow activation energy of KCZ glasses are higher and their dependence on the ZrO_2 content is steeper.

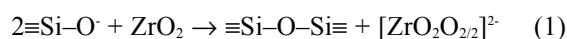
INTRODUCTION

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 heavy elements as 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 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 [2,9].

EXAFS studies of Zr coordination in selected silicate glasses have shown that variations in the local environment of Zr are relatively small [10]. In silicate glasses with lower ZrO_2 concentrations (1-4 wt.%) Farges and Calas [11] found Zr to be mainly 6 coordi-

nated. 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 [12] stated that ZrO_2 is a network-former producing tetrahedral ZrO_4 groups. Furthermore, Linthout [13] 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 [10] on the basis of the EXAFS study consists in ZrO_6 octahedron with four bridging and two non-bridging oxygen atoms (schematically $[ZrO_2O_{2,2}]^2-$). 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:



This situation formally resembles the Al_2O_3 network-forming structural activity where the non-bridging oxygen atoms of partially depolymerized silicate network are consumed by converting the Al_2O_3 to tetrahedral anions $[AlO_{4/2}]^-$ [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 [14-17]. 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 [18]. The literature data concerning the composition - property relationships for more than three component zirconia containing silicate systems are relatively scarce [19,20]. Therefore the effect of the equimolar ZrO_2/SiO_2 substitution in sodium-calcium and potassium-calcium trisilicate glasses $15M_2O.10CaO.xZrO_2.(75-x)SiO_2$ ($M=Na, K, x = 1, 3, 5, \text{ and } 7$) is in the scope of the present work.

EXPERIMENTAL

The glass batches were prepared by mixing of powdered Na_2CO_3 (AFT, p.a.), K_2CO_3 (Fluka, p.a.), $CaCO_3$ (AFT, 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 supercanthal 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.

Thermal expansion coefficient of glass, α_g , together with the glass transition temperature, T_g , were obtained by thermodilatometry (Netzsch, TMA 402) during cooling from sufficiently high temperature by the cooling rate of 5°C/min. The linear thermal expansion coefficient α_g was obtained from the slope of the cooling curve in temperature interval 400-450°C. The experimental data for the NCZ0 glass were obtained in our previous work in the temperature interval 350-450°C.

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 distilled water, CD, was determined on grained sample according to the ISO norm [21] at 98°C. The values are given in cm^3 of 0.01 mol/dm³ hydrochloric acid needed for neutralisation of alkalis leached from 1 g of glass grains.

The low-temperature viscosities between 10^8 and 10^{12} dPa.s were measured by thermo-mechanical ana-

Table 1. The composition and abbreviation of studied glasses (mol. %).

Glass	Na ₂ O	CaO	ZrO ₂	SiO ₂	Glass	K ₂ O	CaO	ZrO ₂	SiO ₂
NCZ0	15	10	0	75					
NCZ1	15	10	1	74	KCZ1	15	10	1	74
NCZ3	15	10	3	72	KCZ3	15	10	3	72
NCZ5	15	10	5	70	KCZ5	15	10	5	70
NCZ7	15	10	7	68	KCZ7	15	10	7	68

Table 2. Measured physical and chemical properties of studied glasses. Average standard error of measurement of density ± 0.0001 g/cm³, thermal expansion coefficient $\pm 1 \cdot 10^{-7}/K^{-1}$ and refractive index ± 0.0001 .

Glass	M_g (g/mol)	ρ^{20} (g/cm ³)	$10^7 \alpha_g$ (K ⁻¹)	T_g (K)	n_D^{20}	R_m (cm ³ /mol)	CD (cm ³)
*NCZ0	59.97	2.4753	95	819	1.5140	7.29	-
NCZ1	60.69	2.5061	96	830	1.5193	7.35	0.690 ± 0.028
NCZ3	62.13	2.5716	94	850	1.5319	7.49	0.292 ± 0.001
NCZ5	63.57	2.6425	85	867	1.5463	7.62	0.225 ± 0.015
NCZ7	65.02	2.7025	-	-	1.5598	7.78	0.167 ± 0.015
KCZ1	65.52	2.4885	103	883	1.5191	7.99	1.325 ± 0.009
KCZ3	66.96	2.5725	104	895	1.5352	8.11	1.192 ± 0.008
KCZ5	68.41	2.6313	-	-	1.5471	8.25	0.675 ± 0.008
KCZ7	69.85	2.6597	-	-	1.5524	8.40	0.275 ± 0.001

*values from previous unpublished work of Chromčíková.

lyzer (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. $5 \times 5 \times 20$ mm) sample with cross-section S :

$$\eta = \frac{G}{3S(d\varepsilon/dt)} \quad (2)$$

RESULTS AND DISCUSSION

The measured values of density, thermal expansion coefficient, glass transition temperature, refractivity index, and chemical durability against water (CD, expressed in cm^3 of 10^{-2} molar HCl [21]) are summarized in table 2 together with the mean molar (formula) weight of glass, M_g , and molar refractivity calculated by:

$$R_m = \frac{(n_D^{20})^2 - 1}{(n_D^{20})^2 + 2} \frac{M_g}{\rho^{20}} \quad (3)$$

In the case of potassium glasses KCZ5 and KCZ7 as well as in the case of the sodium NCZ7 glass the glass transition region was partially above the experimentally accessible temperature range of thermodynamic measurement. Thus, the values of T_g , and α_g were not measured for these glasses. As was expected, the chemical durability steeply increases (i.e. CD decreases) with increasing ZrO_2 content in both kinds of studied glasses. 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. Also the density, glass transition temperature, refractive index and molar refractivity values are positively correlated with ZrO_2 content in both studied compositional series. The steep increase of T_g with increasing ZrO_2 content in silicate glasses was also reported by Takahashi [5], and Fisher [6]. With the

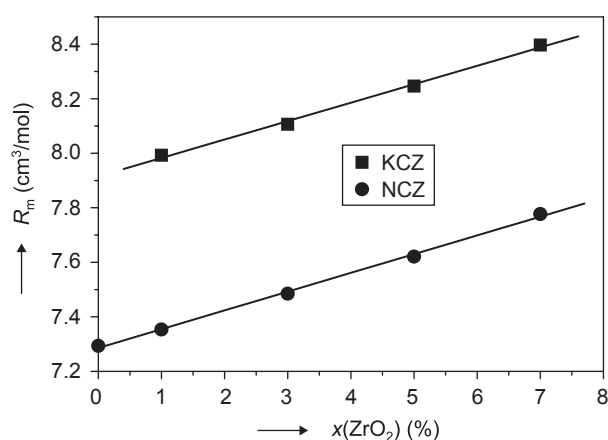


Figure 1. The dependence of molar refractivity on mole fraction of ZrO_2 .

exception of NCZ0 glass, the thermal expansion coefficient of sodium glasses decreases with the increasing ZrO_2 content. Probably the same is true for the potassium glasses, but the insufficient number of experimental data prevents the statistical confirmation of this idea. Similar tendency was confirmed by the work of Kheifets [4]. The thermal expansion coefficients of potassium glasses are about 10% higher in comparison with the sodium ones.

Figure 1 illustrates the dependence of molar refractivity of NCZ and KCZ glasses on ZrO_2 content. It can be seen, that the almost perfect linear (correlation coefficient 0.9991 for NCZ glasses, and 0.9981 for KCZ glasses) correlation is obtained in both cases. The regression line

$$R_{m,NCZ} = [(7.286 \pm 0.007) + (0.0688 \pm 0.0017) \times (\text{ZrO}_2)] \text{ cm}^3/\text{mol} \quad (4)$$

describes the NCZ experimental data with standard deviation of approximation of $0.010 \text{ cm}^3/\text{mol}$. In the case of KCZ glasses the regression equation

$$R_{m,KCZ} = [(7.915 \pm 0.068) + (0.0676 \pm 0.0030) \times (\text{ZrO}_2)] \text{ cm}^3/\text{mol} \quad (5)$$

fits the data with standard deviation of $0.013 \text{ cm}^3/\text{mol}$. The ZrO_2 content in the equations (4,5) is given in mole %. The slope of the regression line corresponds to the increment of molar refractivity caused by substitution of 1 mole % of SiO_2 by ZrO_2 . It is worth noting that in the limits of standard deviation the slope is the same for both glass series.

The temperature dependence of viscosity was described by the Arrhenius-like equation:

$$\log(\eta/\text{dPas}) = A + B/T \quad (6)$$

where A , and B are constants routinely determined by regression analysis, and T is thermodynamic tempera-

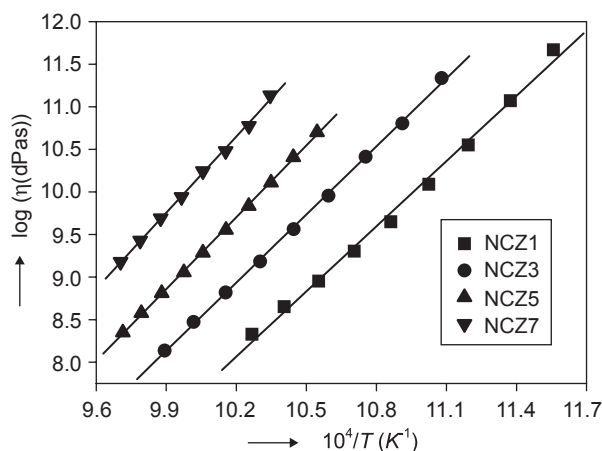


Figure 2. Arrhenius plot of viscosity - temperature dependence for NCZ glasses.

ture. The temperature independent viscous flow activation energy, E_a , was calculated by:

$$E_a = (\partial \ln \eta / \partial (1/T))_P = \ln(10)RB = 2.303RB \quad (7)$$

where R is the molar gas constant.

Experimental values of viscosity are plotted in $\log(\eta/\text{dPa}\cdot\text{s})$ versus $10^4K/T$ coordinate system in figure 2 for NCZ glasses, and in figure 3 for KCZ glasses. It can be concluded that all depicted dependences are linear with the isothermal viscosity value steeply increasing with increasing ZrO_2 content, and with the slope moderately increasing with increasing ZrO_2 content. Table 3 summarizes the values of A , and B coefficients (equation (6)), and the values of activation energy calculated according the equation (7). It can be seen that both A , and B values are increasing with increasing ZrO_2 content in both glass series.

Figure 4 demonstrates the linear dependence of viscous flow activation energy on ZrO_2 mole fraction. For NCZ glasses this can be described with the regression equation:

$$E_a(\text{NCZ}) = [(469 \pm 4) + (14.1 \pm 0.9) \times (\text{ZrO}_2)] \text{ kJ/mol} \quad (8)$$

with correlation coefficient of 0.9957 and standard deviation of approximation of 0.43 kJ/mol. For KCZ glasses the regression equation

$$E_a(\text{KCZ}) = [(529 \pm 12) + (38.3 \pm 4.1) \times (\text{ZrO}_2)] \text{ kJ/mol} \quad (9)$$

was obtained with the correlation coefficient of 0.9943 and standard deviation of approximation of 1.23 kJ/mol. It can be concluded that for KCZ glasses the activation energy is higher and its dependence on ZrO_2 mole fraction is steeper.

CONCLUSION

Increasing content of ZrO_2 significantly improves the chemical durability against water in both studied glass series. The $\text{ZrO}_2/\text{SiO}_2$ substitution strengthens the silicate network and therefore increases the values of glass transition temperature, and viscosity. The thermal expansion coefficient decreases with the increasing ZrO_2 content. Molar refractivity depends linearly on the ZrO_2 content expressed in mole %. The slope of the regression line is the same for both studied glass series, whereas the higher intercept for potassium glasses reflects the greater polarizability of the potassium cation with respect to the Na^+ cation. In comparison with the NCZ glasses both the viscosity and the viscous flow activation energy of KCZ glasses are higher and their dependence on the ZrO_2 content is steeper.

Table 3. Coefficients of the viscosity equation (equation (6)) and viscous flow activation energies (equation (7)) together with standard deviations and standard deviation of $\log \eta$ approximation s_{apr} .

Glass	A	B	E_a (kJ/mol)	$s_{\text{apr}}[\log(\eta \text{ dPa}\cdot\text{s})]$
NCZ1	-17.97 ± 0.76	25526 ± 700	489 ± 13	0.087
NCZ3	-18.26 ± 0.29	26658 ± 279	510 ± 5	0.032
NCZ5	-18.99 ± 0.23	28131 ± 232	539 ± 4	0.020
NCZ7	-19.78 ± 0.51	29839 ± 512	571 ± 10	0.031
KCZ1	-20.26 ± 0.41	29769 ± 401	570 ± 8	0.034
KCZ3	-22.68 ± 0.57	33018 ± 577	632 ± 11	0.028
KCZ5	-26.50 ± 0.57	37940 ± 588	726 ± 11	0.023

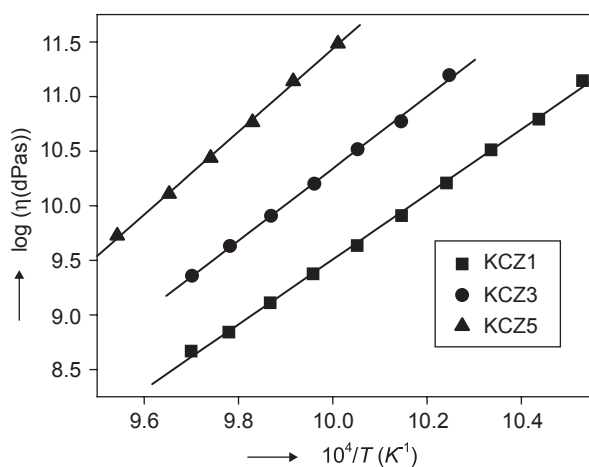


Figure 3. Arrhenius plot of viscosity - temperature dependence for KCZ glasses.

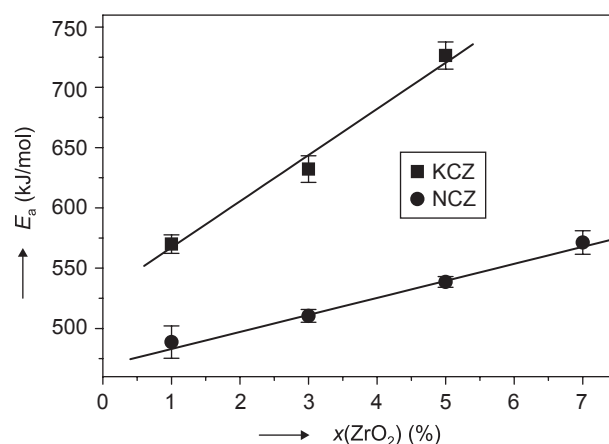


Figure 4. Dependence of viscous flow activation energy on mole fraction of ZrO_2 .

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VLASTNOSTI VYBRANÝCH ZIRKONIČITANO-KREMIČITANOVÝCH SKIEL

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Pre sklá so zložením $15M_2O \cdot 10CaO \cdot xZrO_2 \cdot (75-x)SiO_2$ ($M = Na$ pre NCZ sklá a $M = K$ pre KCZ sklá; $x = 1, 3, 5, a 7$) sa zmerali teplotné závislosti viskozity a hustoty, teplotná rozťažnosť, teplota skleneného prechodu, index lomu, a chemická odolnosť voči vode. V práci sa v súvislosti so zmenami štruktúry kremičitanovej siete diskutuje efekt ekvimolárnej substitúcie SiO_2/ZrO_2 na merané fyzikálne vlastnosti. Potvrdilo sa, že zvyšujúci obsah ZrO_2 výrazne zvyšuje chemickú odolnosť voči vode v oboch skúmaných sériách zložených skiel. Substitúcia SiO_2/ZrO_2 spevňuje kremičitanovú sieť a zvyšuje preto teplotu skleneného prechodu a viskozitu, pričom súčasne znižuje koeficient teplotnej rozťažnosti. Ďalej sa zisťovalo, že molárna refrakcia je lineárnou funkciou obsahu ZrO_2 vyjadreného v molových %. Emranica tejto závislosti je rovnaká v oboch skúmaných sériách zložených skiel, pričom vyšší úsek pozorovaný pre draselné sklá dobre korešponduje s vyššou polarizovateľnosťou draselného katiónu v porovnaní so sodným katiómom. V porovnaní s NCZ sklami majú KCZ sklá vyššie hodnoty viskozity a aktivačnej energie viskózneho toku, pričom lineárna závislosť aktivačnej energie viskózneho toku od obsahu ZrO_2 je pre KCZ sklá strmšia.