# PROPERTIES OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES II.

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*Viscosity, density, thermal expansion, glass transition temperature, refractive index, molar refraction, and chemical durability of $15M_2O{\cdot}10ZnO{\cdot}xZrO_2{\cdot}(75\text{-}x)SiO_2$ (M = Na, K; x = 1, 3, 5, and 7) glasses were measured. The strong influence of $ZrO_2$/$SiO_2$ equimolar substitution on measured physical and chemical properties was detected in accord with the assumption of the glass network strengthening by $ZrO_2$. The effect of ZnO / CaO substitution was quantified by comparison with the results obtained for $15M_2O{\cdot}10CaO{\cdot}xZrO_2{\cdot}(75\text{-}x)SiO_2$ (M = Na, K; x = 1, 3, 5, and 7) glasses. It was demonstrated that the ZnO/CaO substitution strengthens the silicate network.*

## 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 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 $15M_2O\cdot10CaO\cdot xZrO_2\cdot(75\text{-}x)SiO_2$ (M = Na, K, $x$ = 1, 3, 5, and 7) was studied in our previous work [24]. As far as the zinc oxide is used in barium free crystal glasses for improvement of their chemical durability the present paper deals with the equimolar $ZrO_2/SiO_2$ substitution in zinc oxide containing trisilicate glasses $15M_2O\cdot10ZnO\cdot xZrO_2\cdot(75\text{-}x)SiO_2$ (M = Na, K, $x$ = 1, 3, 5, and 7). In couple with our previous work [24] the effect of CaO/ZnO substitution in trisilicate glasses with different degree of $ZrO_2/SiO_2$ exchange can be estimated. The ZnO/CaO substitution is expected to produce effects resulting from the cross-linking of the partially depolymerized silicate network hence the networkforming zinc oxide is substituted for the networkmodifying calcium oxide. But it is a special question how this effect will be influenced with the increasing ratio of $ZrO_2/SiO_2$ substitution.

## 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. Thermal expansion coefficient of glass,  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 $\alpha_g$ was obtained from the slope of the cooling curve in 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 water, *CD*, was determined on grained sample according to the norm [25] at 98°C.

The low-temperature viscosities between $10^8$ and $10^{12}$ dPas were measured by thermo-mechanical analyzer (Netzsch, TMA 402). The viscosity value, $\eta$, 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 $S$:

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

## 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 [25]) are summarized in Table 2 together with the mean molar (formula) weight of glass, $M_g$, and molar refractivity calculated by:

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

Table 1. The composition and abbreviation of studied glasses.

| Glass | $Na_2O$ | ZnO | $ZrO_2$ | $SiO_2$ | Glass | $K_2O$ | ZnO | $ZrO_2$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|
| NzZ0 | 15 | 10 | 0 | 75 | KzZ0 | 15 | 10 | 0 | 75 |
| NzZ1 | 15 | 10 | 1 | 74 | KzZ1 | 15 | 10 | 1 | 74 |
| NzZ3 | 15 | 10 | 3 | 72 | KzZ3 | 15 | 10 | 3 | 72 |
| NzZ5 | 15 | 10 | 5 | 70 | KzZ5 | 15 | 10 | 5 | 70 |
| NzZ7 | 15 | 10 | 7 | 68 | KzZ7 | 15 | 10 | 7 | 68 |

In the case of potassium glasses (with the exception of the KzZ0 and KzZ1 glasses) the glass transition region was partially above the experimentally accessible temperature range of thermodilatometric measurement. Thus, the values of Tg values were not measured for these glasses. For comparison, the results obtained in our previous work [24] for $15M_2O·10CaO·xZrO_2·$ $·(75\text{-}x)SiO_2$ (M = Na, K, x = 1, 3, 5, and 7) are also reported in Table 2. As expected, the chemical durability steeply increases (i.e. CD value 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. When the results are compared with those obtained for calcia containing glasses we can confirm the netwotkforming ability of ZnO leading to significant increase of chemical durability. This effect is more pronounced for lower $ZrO_2$ content.

In overall, e.g. comparing first and the last members of present compositional series, the thermal expansion coefficient decreases with increasing $ZrO_2$ content. Due to presence of networkforming zinc oxide this effect is much less pronounced than for analogous calcia containing glasses (Table 2).

The density, glass transition temperature (when determined), refractive index and molar refractivity values are positively correlated with $ZrO_2$ content in both studied compositional series. The increase of $T_g$ with increasing $ZrO_2$ content in silicate glasses was also reported by Takahashi [5], and Fisher [6]. The thermal expansion coefficient of sodium glasses slightly 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 situation is similar to those of CaO containing glasses (Table 2), thus the ZnO/CaO substitution does not significantly change the absolute values of the above quantities and also their dependence on the degree of $ZrO_2/SiO_2$ substitution.

Figure 1 illustrates the dependence of molar refractivity of NzZ and KzZ glasses on $ZrO_2$ content. It can be seen, that the almost perfect linear (correlation coefficient 0.9935 for NzZ glasses, and 0.9942 for KzZ glasses) correlation is obtained in both cases. The regression line

$$R_{m,NzZ} = [(7.243 \pm 0.017) + (0.0641 \pm 0.0042)\, x(ZrO_2)]\ \text{cm}^3/\text{mol} \quad (5)$$

describes the NzZ experimental data with standard deviation of approximation of 0.024 cm$^3$/mol. In the case of KzZ glasses the regression equation

$$R_{m,KzZ} = [(7.845 \pm 0.015) + (0.0585 \pm 0.0038)\, x(ZrO_2)]\ \text{cm}^3/\text{mol} \quad (6)$$

fits the data with standard deviation of 0.021 cm$^3$/mol. The $ZrO_2$ content, $x(ZrO_2)$, in the Equations (5-8) 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

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

| Glass | $M_g$ (g/mol) | $\rho^{20}$ (g/cm$^3$) | $10^7\ \alpha_g$ (K$^{-1}$) | $T_g$ (K) | $n_D^{20}$ | $R_m$ (cm$^3$/mol) | $CD$ (cm$^3$) |
|---|---|---|---|---|---|---|---|
| NzZ0 | 62.50 | 2.559 ± 0.001 | 91 | 794 | 1.5072 | 7.27 | 0.245 ± 0.013 |
| NCZ0 | 59.97 | 2.475 ± 0.001 | 95 | 807 | 1.5140 | 7.29 | - |
| NzZ1 | 63.13 | 2.635 ± 0.002 | 94 | 810 | 1.5202 | 7.29 | 0.234 ± 0.008 |
| NCZ1 | 60.69 | 2.506 ± 0.001 | 96 | 830 | 1.5193 | 7.35 | 0.690 ± 0.028 |
| NzZ3 | 64.39 | 2.704 ± 0.007 | 81 | 837 | 1.5345 | 7.41 | 0.140 ± 0.013 |
| NCZ3 | 62.13 | 2.572 ± 0.001 | 94 | 850 | 1.5319 | 7.49 | 0.292 ± 0.001 |
| NzZ5 | 65.65 | 2.738 ± 0.001 | 79 | 851 | 1.5438 | 7.57 | 0.084 ± 0.013 |
| NCZ5 | 63.57 | 2.643 ± 0.001 | 85 | 867 | 1.5463 | 7.62 | 0.225 ± 0.015 |
| NzZ7 | 66.92 | 2.830 ± 0.002 | 80 | 862 | 1.5638 | 7.70 | 0.041 ± 0.013 |
| NCZ7 | 65.02 | 2.703 ± 0.001 | - | - | 1.5598 | 7.78 | 0.167 ± 0.015 |
| KzZ0 | 67.33 | 2.570 ± 0.003 | 94 | 852 | 1.5111 | 7.85 | 0.835 ± 0.044 |
| KCZ0 | 64.80 | 2.478 ± 0.001 | 103 | 860 | - | - | - |
| KzZ1 | 67.96 | 2.613 ± 0.001 | 98 | 841 | 1.5178 | 7.88 | 0.630 ± 0.037 |
| KCZ1 | 65.52 | 2.489 ± 0.001 | 103 | 883 | 1.5191 | 7.99 | 1.325 ± 0.009 |
| KzZ3 | 69.23 | 2.635 ± 0.001 | 85 | | 1.5245 | 8.04 | 0.402 ± 0.014 |
| KCZ3 | 66.96 | 2.573 ± 0.001 | 104 | 895 | 1.5352 | 8.11 | 1.192 ± 0.008 |
| KzZ5 | 70.49 | 2.737 ± 0.002 | 90 | | 1.5453 | 8.15 | 0.359 ± 0.033 |
| KCZ5 | 68.41 | 2.631 ± 0.001 | - | - | 1.5471 | 8.25 | 0.675 ± 0.008 |
| KzZ7 | 71.75 | 2.804 ± 0.001 | 86 | - | 1.5574 | 8.24 | 0.113 ± 0.034 |
| KCZ7 | 69.85 | 2.660 ± 0.001 | - | - | 1.5524 | 8.40 | 0.275 ± 0.001 |

noting that in the limits of standard deviation the slope is the same for both glass series. In our previous work [24], following regression equations were obtained for CaO containing glasses:

$$R_{m,NCZ} = [(7.286 \pm 0.07) + (0.0688 \pm 0.0017)\, x(ZrO_2)]\ \text{cm}^3/\text{mol} \tag{7}$$

describing the NCZ experimental data with standard deviation of approximation of 0.010 cm$^3$/mol, and

$$R_{m,KCZ} = [(7.915 \pm 0.068) + (0.0676 \pm 0.0030)\, x(ZrO_2)]\ \text{cm}^3/\text{mol} \tag{8}$$

that fits the data with standard deviation of 0.013 cm$^3$/mol. It can be concluded that the higher polarizability of Zn(II) increases slightly both the slope and the intercept in sodium and potassium glasses.

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

$$\log (\eta/\text{dPa.s}) = A + B/T \tag{9}$$

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

$$E_a = [\partial \ln \eta/\partial(1/T)]_P = \ln(10)RB = 2.303\ RB \tag{10}$$

where $R$ is the molar gas constant.

Experimental values of viscosity are plotted in log ($\eta$/dPa.s) versus 10$^4$ K/$T$ coordinate system in Figure 2 for NzZ glasses, and in Figure 3 for KzZ glasses. It can be concluded that all depicted dependences are linear with the isothermal viscosity value steeply increasing

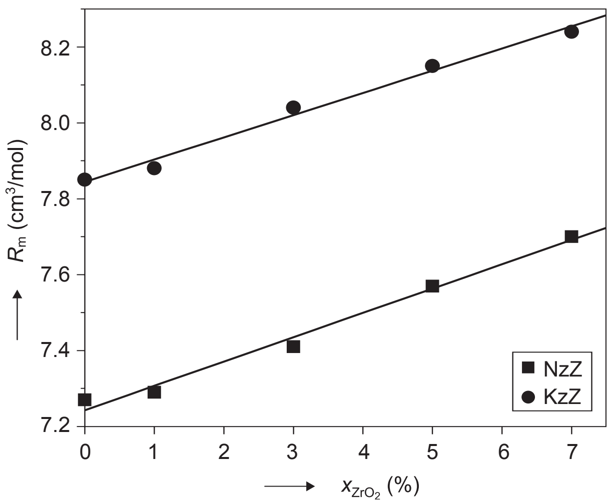


Figure 1. The dependence of molar refractivity on mole fraction of $ZrO_2$.

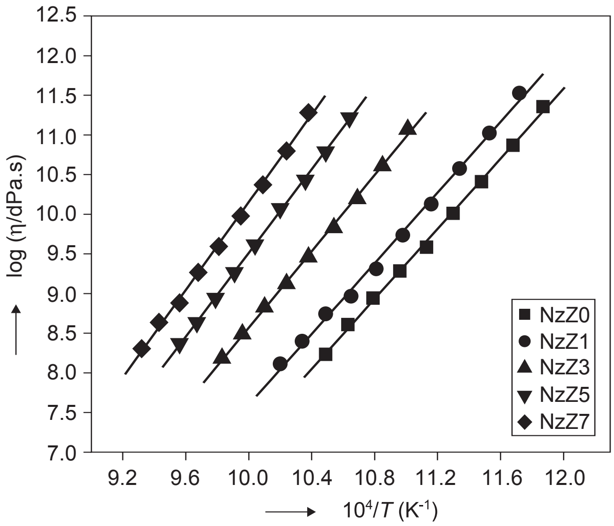


Figure 2. Arrhenius plot of viscosity - temperature dependence for NzZ glasses.

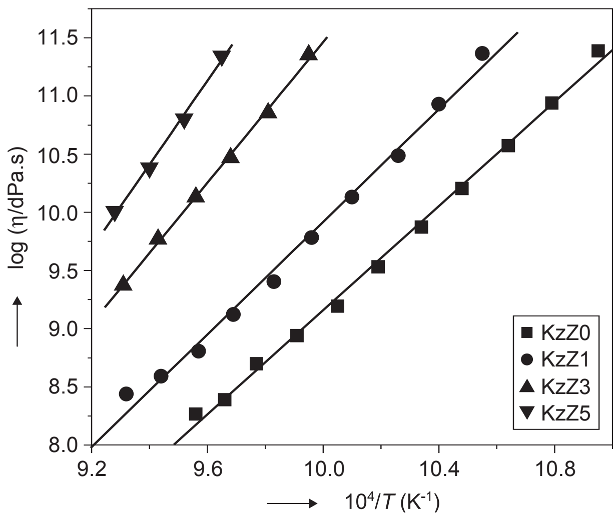


Figure 3. Arrhenius plot of viscosity - temperature dependence for KzZ glasses.

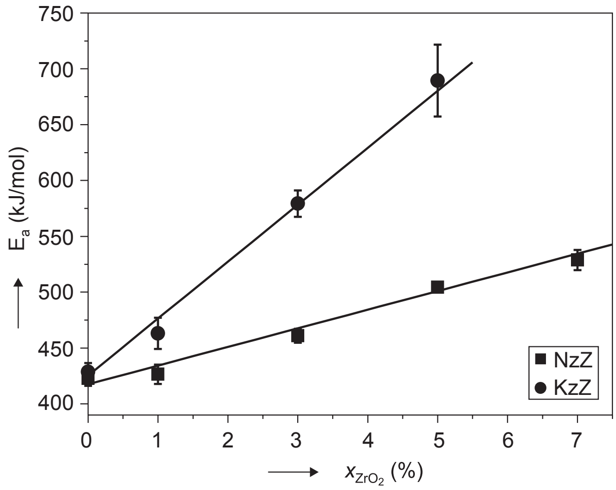


Figure 4. Dependence of viscous flow activation energy on mole fraction of $ZrO_2$.

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 (9), and the values of activation energy calculated according the Equation (10). It can be seen that both A, and B values are increasing with increasing $ZrO_2$ content in both glass series.

The viscous flow activation energy of calcia containing glasses ($15M_2O\cdot 10CaO\cdot xZrO_2\cdot(75\text{-}x)SiO_2$, M = = Na/K) is higher when compared with zinc oxide containing glasses. However the *A* values of NCZ and KCZ glasses are lower when compared with those of NzZ and KzZ glasses. Thus the viscosity difference is not as high as can be expected on the basis of the *B* values. In another words, there exist some particular temperature where the MzZ and MCZ (M = Na, K) viscosity curves intersects. However, this temperature can be out of range of the validity of the simple Andrade's equation.

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

$$E_a\,(\text{NzZ}) = [(418 \pm 5) + (16.7 \pm 1.2)\; x(ZrO_2)]\ \text{kJ/mol} \qquad (11)$$

with correlation coefficient of 0.9903 and standard deviation of approximation of 1.10 kJ/mol. For KzZ glasses the regression equation

$$E_a\,(\text{KzZ}) = [(425 \pm 7) + (51.0 \pm 4.1)\; x(ZrO_2)]\ \text{kJ/mol} \qquad (12)$$

was obtained with the correlation coefficient of 0.9964 and standard deviation of approximation of 0.75 kJ/mol. It can be concluded that for KzZ glasses the activation energy is higher and its dependence on $ZrO_2$ mole fraction is steeper. Both the slopes and the values of activation energy for studied glasses are higher than those for CaO glasses where the following relationships were found by regression analysis [24]:

$$E_a\,(\text{NCZ}) = [(469 \pm 4) + (14.1 \pm 0.9)\; x(ZrO_2)]\ \text{kJ/mol} \qquad (13)$$

$$E_a\,(\text{KCZ}) = [(529 \pm 12) + (38.3 \pm 4.1)\; x(ZrO_2)]\ \text{kJ/mol} \qquad (14)$$

## CONCLUSIONS

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. 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 higher intercept for potassium glasses reflects the greater polarizability of potassium cation with respect to the $Na^+$ cation. In comparison with NzZ glasses both the viscosity and viscous flow activation energy of KzZ glasses are higher and their dependence on $ZrO_2$ content is steeper. When compared with analogous calcium oxide glasses the networkforming activity of ZnO is demonstrated by increase of viscosity, chemical dura-

Table 3. Coefficients of the viscosity Equation (9) and viscous flow activation energies (Equation 10) together with standard deviations and standard deviation of log $\eta$ approximation $s_{apr}$. The values for analogical lime glasses NCZx and KCZx (taken from [24]) are reported for comparison.

| Glass | *A* | *B* | $E_a$ (kJ/mol) | $s_{apr}$[log($\eta$/(dPas)] |
|---|---|---|---|---|
| NzZ0 | -14.92 ± 0.38 | 22083 ± 342 | 423 ± 7 | 0.046 |
| NCZ0 | -19.02 ± 0.82 | 25551 ± 729 | 489 ± 14 | 0.100 |
| NzZ1 | -14.68 ± 0.50 | 22278 ± 453 | 426 ± 9 | 0.070 |
| NCZ1 | -17.97 ± 0.76 | 25526 ± 700 | 489 ± 13 | 0.087 |
| NzZ3 | -15.52 ± 0.34 | 24084 ± 328 | 461 ± 6 | 0.038 |
| NCZ3 | -18.26 ± 0.29 | 26658 ± 279 | 510 ± 5 | 0.032 |
| NzZ5 | -16.83 ± 0.21 | 26347 ± 208 | 504 ± 4 | 0.022 |
| NCZ5 | -18.99 ± 0.23 | 28131 ± 232 | 539 ± 4 | 0.020 |
| NzZ7 | -17.47 ± 0.47 | 27621 ± 478 | 529 ± 9 | 0.049 |
| NCZ7 | -19.78 ± 0.51 | 29839 ± 512 | 571 ± 10 | 0.031 |
| KzZ0 | -13.23 ± 0.43 | 22387 ± 418 | 429 ± 8 | 0.062 |
| KCZ0 | -20.56 ± 0.68 | 29308 ± 653 | 561 ± 13 | 0.067 |
| KzZ1 | -14.27 ± 0.73 | 24190 ± 736 | 463 ± 14 | 0.092 |
| KCZ1 | -20.26 ± 0.41 | 29769 ± 401 | 570 ± 8 | 0.034 |
| KzZ3 | -18.80 ± 0.59 | 30261 ± 617 | 579 ±12 | 0.033 |
| KCZ3 | -22.68 ± 0.57 | 33018 ± 577 | 632 ± 11 | 0.028 |
| KzZ5 | -23.44 ± 1.59 | 36013 ± 168 | 689 ± 32 | 0.046 |
| KCZ5 | -26.50 ± 0.57 | 37940 ± 588 | 726 ± 11 | 0.023 |

bility, and the decrease of viscous flow activation energy. The difference between ZnO and CaO containing glasses decreases with increasing degree of $ZrO_2/SiO_2$ substitution.

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## VLASTNOSTI VYBRANÝCH ZIRKONIČITANOVÝCH SKIEL II.

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Výroba skla prebieha v rozsiahlom teplotnom intervale, pričom je dôležité poznať chovanie sa skla pri rôznych teplotách, ako aj poznať a predvídať vlastnosti skla so zmenou zloženia. V tejto práci sa prezentujú niektoré fyzikálne a chemické vlastnosti skiel zloženia $15M_2O{\cdot}10ZnO{\cdot}xZrO_2{\cdot}(75\text{-}x)SiO_2$ (M = Na, K, x = 1, 3, 5 a 7). Potvrdilo sa, že ekvimolárná substitúcia $ZrO_2/SiO_2$ veľmi ovplyvňuje merané fyzikálne a chemické vlastnosti. Vplyv ZnO/CaO ekvimolárnej substitúcie bol kvantitatívne porovnaný s výsledkami získanými pre $15M_2O{\cdot}10CaO{\cdot}xZrO_2{\cdot}(75\text{-}x)SiO_2$ (M = Na, K; x = 1, 3, 5 a 7) sklá. Ukázalo sa, že ZnO/CaO substitúcia spevňuje kremičitanovu sieť.