Sborník vědeckých prací Vysoké školy báňské – Technické univerzity Ostrava
číslo 1, rok 2008, ročník LI, řada hutnická
článek č. 1400

PROPERTIES OF SELECTED ZIRCONIA CONTAINING SILICATE GLASSES

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ABSTRACT: Viscosity, density, thermal expansion, glass transition temperature, refractive index, molar refraction, and chemical durability of compositional series of Na_2O-K_2O-ZnO-CaO-ZrO_2-SiO_2 glasses containing 1 and 3 mol. % ZrO_2 were measured and interpreted according to the network-forming / modifying activities of particular oxides. The influence of ZrO_2 / SiO_2, ZnO / CaO, and K_2O / Na_2O substitution on measured physical and chemical properties was detected. The regression formulae describing the temperature and composition dependence of the above properties were proposed.

KEY WORDS: density, zirconia-silicate glasses

1. INTRODUCTION

The tendency to produce crystal glass without toxic elements like BaO and PbO is observed in recent years. The most suitable elements to substitute harmful oxides belong to fourth group of periodical table (e.g. ZrO_2 and TiO_2). Addition of ZrO_2 has positive influence on hydrolytic durability, refractive index and density of glasses. On the other hand, it increases the glass transition temperature and viscosity thereby increases the melting temperature [1, 2]. In silicate glasses with lower ZrO_2 amount (1-4 wt. %) Farges and Calas [3] found Zr to be mainly 6coordinated. The abundance of 6-coordinated Zr should increase with melt depolymerization as a result of the increasing network modifier content. The possible structural model of 6coordinated zirconium in silicate glasses based on the EXAFS study [4] consists in ZrO_6 octahedron with four bridging and two non-bridging oxygen atoms (schematically $[ZrO2O4/2]^{4-}$). 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:

$$4 \equiv Si\text{-}O\text{-} + ZrO_2 \rightarrow 2 \equiv Si\text{-}O\text{-}Si \equiv + [ZrO_2O_{4/2}]_4\text{-} \qquad (1)$$

The literature data concerning the composition - property relationships for more than three component zirconia containing silicate systems are relatively scarce [5, 6]. Therefore the effect of the equimolar ZrO_2 / SiO_2, ZnO / CaO, and K_2O / Na_2O substitution in the Na_2O-K_2O-CaO-ZnO-ZrO_2-SiO_2 system is aimed in the present work.

2. EXPERIMENTAL PART

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 re nain there until completely cool. Theoretical composition and abbreviation of glass samples is summarized in Tab.1.

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

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

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^{-1}. The linear thermal expansion coefficient αg 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 ČSN ISO 70 0531 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 x 5 mm x 20 mm) sample with cross-section *S*:

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

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) are summarized in Tab.2 together with the molar (formula) weight of glass, Mg, and molar refractivity calculated by:

$$R_m = \frac{\left(n_D^{20}\right)^2 - 1}{\left(n_D^{20}\right)^2 + 2} \frac{M_g}{\rho^{20}}. \qquad (3)$$

Tab.2: Measured properties of studied glasses. Average standard error of measurement of density - ± 0.0003 g.cm^{-3} thermal expansion coefficient - ± 1·10^{-7}/K, and refractive index ± 0.001.

Glass	M_g [g.mol^{-1}]	ρ_{20} [g.cm^{-3}]	$10^7\alpha_g$ [K^{-1}]	T_g [K]	n_D^{20}	R_m [cm^3.mol^{-1}]	CD [cm^3]
NCzZ1	61.86	2.5576	76	807	1.518	7.33	0.262±0.031
KCzZ1	66.70	2.5361	89	864	1.515	7.93	0/652±0.097
NKCZ1	63.02	2.5053	104	828	1.519	7.64	0.520±0.024
NKzZ1	65.55	2.6001	94	817	1.516	7.62	0.128±0.018
NKCzZ1	64.28	2.5538	85	823	1.518	7.63	0.233±0.014
NCzZ3	63.13	2.6282	82	826	1.532	7.44	0.254±0.037
KCzZ3	67.96	2.5893	86	871	1.525	8.04	0.329±0.034
NKCZ3	64.28	2.5705	101	855	1.530	7.72	0.253±0.037
NKzZ3	66.81	2.6614	88	827	1.528	7.73	0.171±0.007
NKCzZ3	65.54	2.6195	97	833	1.532	7.75	0.118±0.011

The viscosity temperature dependence (Figs. 1 and 2) was described by the Arrhenius-like equation (also known as Andrade's equation):

$$\log(\eta / \mathrm{dPa.s}) = A + B/T, \tag{4}$$

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

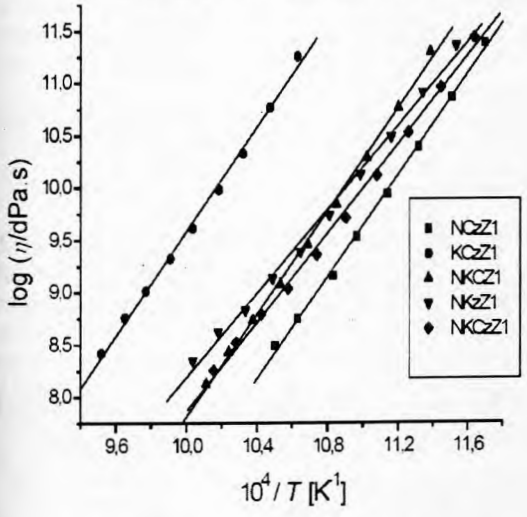

Fig. 1: Arrhenius plot of viscosity - temperature

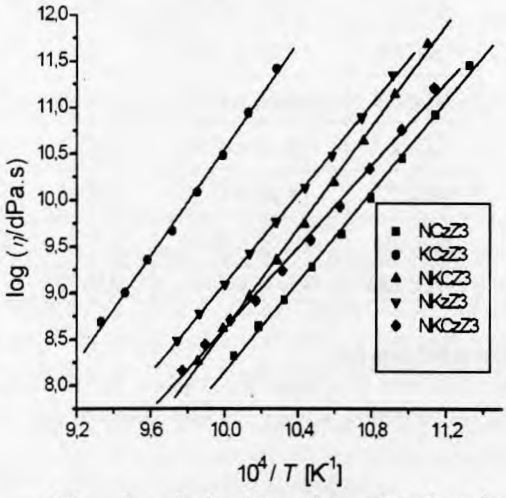

Fig. 2: Arrhenius plot of viscosity - temperature dependence for glasses containing 1mol. % ZrO_2 dependence for glasses containing 3mol.% ZrO_2

was calculated by:

$$E_a = \left(\frac{\partial(\ln\eta)}{\partial(1/T)}\right)_p, R = \ln(10)RB2.303RB, \tag{5}$$

where R is the molar gas constant.
It can be seen (Figs. 1 and 2) that the viscosity temperature dependence is correctly described by the Arrhenius-like equation (4) corresponding to the constant value of viscous flow activation energy.

4. CONCLUSIONS

Increasing content of ZrO_2 increases the values of glass density, refractive index, molar refraction, chemical durability, transformation temperature, viscosity and viscous flow activation energy. The same effect can be observed for the ZnO / CaO substitution. Both these trends are in harmony with the higher network forming activity of ZrO_2, and ZnO, respectively. The K_2O / Na_2O substitution makes the glass shorter. Increasing content of ZrO_2 increases the values of glass density, refractive index, molar refraction, chemical durability, transformation temperature, viscosity and viscous flow activation energy. The same effect can be observed for the ZnO / CaO substitution. Both these trends are in harmony with the higher network forming activity of ZrO_2, and ZnO, respectively. The K_2O / Na_2O substitution makes the glass shorter.

Tab. 3: Coefficients of the viscosity equation (Eq.(4)) and viscous flow activation energies (Eq.(5)) together with standard deviations and standard deviation of logη approximation s_{apr}.

Glass	A	B	Ea / kJ.mol^{-1}	s_{apr}[log(η /dPa.s)]
NCzZ1	-17.11 ± 0.47	24318 ± 428	466 ± 8	0.048
KCzZ1	-15.39 ± 0.57	24969 ± 566	478 ± 11	0.061
NKCZ1	-16.82 ± 0.43	24622 ± 398	471 ± 8	0.049
NKzZ1	-11.88 ± 0.53	20067 ± 493	384 ± 9	0.074
NKCzZ1	-13.43 ± 0.46	21296 ± 421	408 ± 8	0.063
NCzZ3	-16.10 ± 0.47	24244 ± 441	464 ± 8	0.055
KCzZ3	-18.22 ± 0.53	28770 ± 545	551 ± 10	0.048
NKCZ3	-18.68 ± 0.38	27283 ± 361	522 ± 7	0.044
NKzZ3	-15.03 ± 0.19	24124 ± 187	462 ± 4	0.021
NKCzZ3	-13.41 ± 0.49	22020 ± 466	422 ± 9	0.065

Acknowledgement
This work was supported by Agency for Promotion Research and Development under the contract APVV-20-P06405, and by the Slovak Grant Agency for Science under the grant VEGA 1/3578/06.

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