THE PROPERTIES OF THE GLASSES
IN THE Na_2O-K_2O-CaO-BaO-SiO_2 SYSTEM

PETER ŠIMURKA, MAREK LIŠKA*, JOZEF ANTALÍK**

LR CRYSTAL, j.s.c.,
020 61 Lednické Rovne, Slovak Republic

*Joint Glass Labs of Faculty of Industrial Technologies,
University Trenčín and Institute of Inorganic Chemistry of SAS,
M. Rázusa 10, 911 01 Trenčín, Slovak Republic
E-mail: liska@uach1.savba.sk

**Faculty of Chemical Technology, Slovak Technical University,
Radlinského 9, 812 37 Bratislava, Slovak Republic

The viscosity, liquidus and glass transition temperatures, refractive index, and the hydrolytic resistance are reported for 15 glass samples of the title glass system. Using the non-linear regression analysis, the temperature and compositional dependence of viscosity was expressed by the mixed polynomial representation (of the individual oxides mole fractions) of the A, B and T_0 coefficients of the Vogel-Fulcher-Tammann equation. The compositional dependencies of the other properties studied were described by the mixed polynomials of both the weight and mole fractions of individual oxides. The obtained results were used in two ways i) the glass composition optimization with respect to the lowering of the stemware glass production cost; ii) the structural role of the individual oxides estimation based on their influence on the studied properties. The present work illustrates the possibility and methodology of the simultaneous use of the same experimental data set for both technological and fundamental research.

INTRODUCTION

The scope of the present work resulted from the need of the stemware glass chemical composition optimization. Thus the aim was to determine the weight fractions of the CaO, BaO, Na_2O, K_2O and SiO_2 oxides in the glass batch. The series of 15 glass compositions resulting from the simplex scheme [1] was proposed. The following ranges of individual oxides content (wt.%) were chosen: 5-10 % CaO, 3.5 - 8.5 % BaO, 10.5 - 15.5 % Na_2O, 3.5 - 8.5 % K_2O, and 72.5 % SiO_2. Besides viscosity the other properties relevant to the stemware glass production are the liquidus and transformation temperatures, refractive index, and hydrolytic resistance [2]. The prerequisite condition to solve this problem is the knowledge of the compositional dependence of all the above mentioned properties.

The technological needs directed the optimization to be done in the weight fractions of individual glass components. Although this requirement is quite acceptable the mole fractions were used in the case of viscosity, where the usage of weight fractions resulted in enormous complexity of the approximation polynomials used for the description of A, B and T_0 compositional dependence. On the other hand some structural information may be extracted only from the functional

dependencies expressed in the mole fractions of individual oxides. That is why, the polynomials describing the property-composition relationships are presented twice in this work. However, between these two representations there is no one to one correspondence. The best possible interpolation is required in the "technological" representation. Thus maximum value of the Fisher's F statistics (inversely proportional to the residual sum of squares) was the only criterion for choosing the optimal polynomials in this case. In the second case only the statistically significant terms can be considered to prevent the artificial corruption of structural implications. Of course, all the means of advanced statistics have to be used to confirm the significance of the regression model proposed in this case [3].

EXPERIMENTAL PART

Batches were prepared from industrial raw materials commonly used for the glass batch preparation - glass sand, limestone, potash, soda ash, and barium carbonate. Antimony oxide, sodium chloride, sodium sulphate, and sodium nitrate were added in analogy with the industrial glass melting. The constant amounts of these minor components were not explicitly considered in the regression models. The glass batches were melted in

ambient atmosphere in a superkanthal furnace at 1500 °C in a Pt-10%Rh crucible. Homogeneity was ensured by hand mixing of the glass melt. Each melt was poured from the crucible onto the stainless steel plate. The glass samples were then tempered in a muffle furnace for twenty minutes at 520 °C, then the furnace was switched off and the samples remained there until reaching the room temperature. The chemical composition was determined after the samples were decomposed in HF and H_2SO_4 solution by the atomic absorption spectroscopy (Na_2O, K_2O, and CaO) and by the gravimetry (BaO as $BaSO_4$). The obtained chemical compositions are summarized in table 1.

Table 1. Chemical compositions of the glass samples investigated, OG -old glass composition (wt.%).

Glass	w(CaO)	w(BaO)	w(Na_2O)	w(K_2O)	w(SiO_2)
1	9.80	3.63	10.37	3.83	72.37
2	4.98	8.47	10.51	3.71	72.33
3	4.96	3.53	10.57	8.59	72.35
4	5.06	3.76	15.28	3.76	72.14
5	7.48	5.67	10.20	3.60	73.05
6	7.29	3.42	10.28	5.97	73.04
7	7.31	3.47	12.60	3.65	72.97
8	5.06	5.99	10.31	6.03	72.61
9	5.06	5.94	12.66	3.75	72.59
10	5.02	3.42	12.36	6.06	73.14
11	6.60	5.03	10.65	5.28	72.44
12	6.54	5.00	12.24	3.58	72.64
13	6.37	3.41	12.18	5.26	72.78
14	4.99	5.24	12.20	5.35	72.22
15	6.28	4.88	11.68	4.82	72.34
OG	5.32	4,56	10,51	6,49	73,12

The low temperature viscosity between 10^7 - 10^{12} dPa s were determined from the axial deformation rate measured by a thermo-mechanical analyzer (Netzsch TMA-402) [4]. The viscosity between 100 - $10^{6.5}$ dPa s were measured by the concentric cylinder rotation viscometer [5]. The liquidus temperature was determined by keeping the sample of coarsely ground glass in a Pt-30%Rh boat in a gradient furnace for 24 hours. The temperature at which the first crystal appeared in the sample was taken as the liquidus temperature. The transformation temperature was determined from the dilatometric cooling curve measured by the TMA-402 with the cooling rate of 5 °C min⁻¹. The refractive index of polished glass samples was measured by the Abbe refractometer using mono-bromnaphtalene as an immersion liquid. The hydrolytic resistance was quantified according to ČSN ISO 719 (i.e. ISO 719 85).

The experimental results are summarized in table 2.

Table 2. Experimental results: T_g - glass transformation temperature, T_l - liquidus temperature, n_D - refractive index, W_R - hydrolytic resistance (HCl solution c = 0.01 mol l⁻¹), and A, B, T_0 - coefficients of Vogel-Fulcher-Tammann viscosity equation, OG -old glass composition.

glass	T_g (°C)	T_l (°C)	n_D	W_R (ml)	A (K)	B (K)	T_0
1	544	994	1.5212	0.54	-1.962	4529	254
2	506	1118	1.5152	0.58	-1.997	4991	189
3	488	869	1.5145	1.61	-1.634	4413	209
4	502	876	1.5105	1.76	-1.623	4265	214
5	547	1087	1.5163	0.55	-1.964	5040	201
6	551	892	1.5142	0.72	-1.813	4629	224
7	515	979	1.5153	0.79	-1.968	4684	216
8	504	956	1.5123	0.89	-1.799	4913	178
9	512	1030	1.5132	0.96	-1.689	4593	199
10	488	884	1.5103	1.81	-1.808	4589	197
11	522	1004	1.5133	0.54	-1.892	4895	205
12	522	1018	1.5154	0.67	-1.930	4667	220
13	521	848	1.5124	0.83	-1.877	4523	224
14	494	989	1.5116	1.18	-1.784	4740	193
15	520	910	1.5156	0.79	-2.004	4683	210
OG	509	962	1,5116	1,03	-1.813	4664	199

TECHNOLOGICAL APPLICATION

Using the standard least squares method the following relationships were found for individual studied properties:

$$T_g (°C) = 805 - 3.429\ w(Na_2O)\ w(K_2O) - 23.22\ w(BaO) - 29.39\ w(CaO) + 4.293\ w(CaO)\ w(K_2O) + 2.382\ w(CaO)\ w(BaO) \quad (1)$$

$$T_l (°C) = 1775 - 49.94\ w(Na_2O) + 16.81\ w(CaO) - 11.361\ w(CaO)\ w(K_2O) \quad (2)$$

$$n_D = 1.4566 + (5.808\ w(K_2O) - 0.335\ w(BaO)\ w(K_2O) + 0.322\ w(BaO)\ w(Na_2O) + 5.525\ w(CaO) - 0.508\ w(CaO)\ w(K_2O)).10^{-3} \quad (3)$$

$$W_R (ml) = 11.78 - 0.0541\ w(K_2O) -1.2313\ w(BaO) + 0.03319\ [w(BaO)]^2 - 2.0115\ w(CaO) + 0.11437\ w(CaO)\ w(BaO) + 0.09021\ [w(CaO)]^2 \quad (4)$$

where T_g is glass transition temperature, T_l - liquidus temperature, n_D - refractive index, W_R - hydrolytic resistance, and w(i) - content oxide i expressed in (wt.%).

$$log(\eta(dPa\ s)) = A + B / (T - T_0) \quad (5)$$

$$A = -14.721 + 54.41 \, x(CaO) + 51.95 \, x(BaO) + 49.34 \, x(Na_2O) + 72.58 \, x(K_2O) \tag{6}$$

$$B \text{ (K)} = 24756.1 - 86687 \, x(CaO) - 69935 \, x(BaO) - 78722 \, x(Na_2O) - 108444 \, x(K_2O) \tag{7}$$

$$T_0 \text{(K)} = -863.5 + 6504 \, x(CaO) + 5100 \, x(BaO) + 4914 \, x(Na_2O) + 6828 \, x(K_2O) \tag{8}$$

where x are mole fractions of individual oxides, and T is the thermo-dynamic temperature.

The equations (1-8) were used for the optimization of stemware glass composition. The new glass composition proposed was identical with the composition of the glass No.15. The comparison between measured and calculated (using equations (1-8)) values for the new and old glass compositions is presented in table 3. Small differences between the calculated and experimental values confirm the validity of the proposed regression models (equations (1-8)). With the proposed new glass composition the batch cost was lowered by about 9 %, melting temperature was lowered by roughly 10 °C, while the key properties determining the glass quality were maintained at the same level, or slightly improved.

$$W_R \text{ (ml)} = 6.75 - 49.1 \, x(BaO) - 109.4 \, x(CaO) + 546 \, [x(CaO)]^2 \tag{12}$$

From the structural point of view, the studied glass system consists of only one network-forming oxide (SiO_2), while the other glass components are the typical network-modifiers. In analogy with the theory of thermodynamic partial molar quantities the influence of each glass component may be rationalized in two ways. First, the partial derivative $d_y(i)$ of the respective physical quantity y with respect to the mole fractions $x(i)$ of oxide i (i $\equiv$ CaO, BaO, Na_2O, and K_2O) reflects the effect of equimolar substitution of oxide i for SiO_2. Second, the "partial molar quantities" $V_y(i)$ reflect the contributions of all the oxides to the quantity y in the following manner [6]:

$$y = x(CaO).V_y(CaO) + x(BaO).V_y(BaO) + x(Na_2O).V_y(Na_2O) + x(K_2O).V_y(K_2O) + x(SiO_2).V_y(SiO_2) \tag{13}$$

All the mentioned quantities calculated for the composition of the glass No.15 (the glass situated in the center of the studied glass compo-sitional region) are

Table 3. The comparison between measured and calculated (using equations (1-8)) values for the new and old glass composition.

Glass	T_g (°C)		T_l (°C)		n_D		W_R (ml)	
	clc.	Δ	clc.	Δ	clc.	Δ	clc.	Δ
OLD	515	6	947	-15	1.5117	0.0001	1.13	0.10
NEW	517	-3	953	43	1.5144	-0.0012	0.73	-0.06

clc. - calculated, Δ - calculated - experimental

STRUCTURAL IMPLICATIONS

Using the standard least squares method [3] the following relationships were found for the property-composition dependencies in the mole fractions representation:

$$T_g \text{(°C)} = 3270 - 88121 \, [x(K_2O)]^2 - 49041 \, x(Na_2O) + 142599 \, x(Na_2O) \, x(K_2O) + 137153 \, [x(Na_2O)]^2 + 68474 \, x(BaO) - 649541 \, x(BaO) \, x(K_2O) - 681390 \, [x(BaO)]^2 - 11568 \, x(CaO) + 154050 \, x(CaO) \, x(Na_2O) - 332188 \, x(CaO) \, x(BaO) \tag{9}$$

$$T_l \text{ (°C)} = 2001 - 5902 \, x(Na_2O) - 154203 \, x(CaO) \, x(K_2O) \tag{10}$$

$$n_D = 1.5093 + 0.9578 \, [x(CaO)]^2 \tag{11}$$

summarized in figures 1-4 and in tables 4 and 5. On the base of these values some structural information related to the studied configuration subspace may be obtained.

The partial derivatives, d_y, and partial molar contributions V_y to the transformation temperature, liquidus temperature, refractive index, and hydrolytic resistance are summarized in table 4. The obtained V_y values have no individual physical meaning. They simply represent some multilinear description of the studied dependence in the vicinity of the glass No.15 composition.

Transformation temperature

The greatest influence of BaO/SiO_2 substitution on T_g decrease can be deduced from the $d_{T_g}(BaO)$ value. Potassium and sodium oxides act in the same manner, but with lower intensity. These results are in accord with the
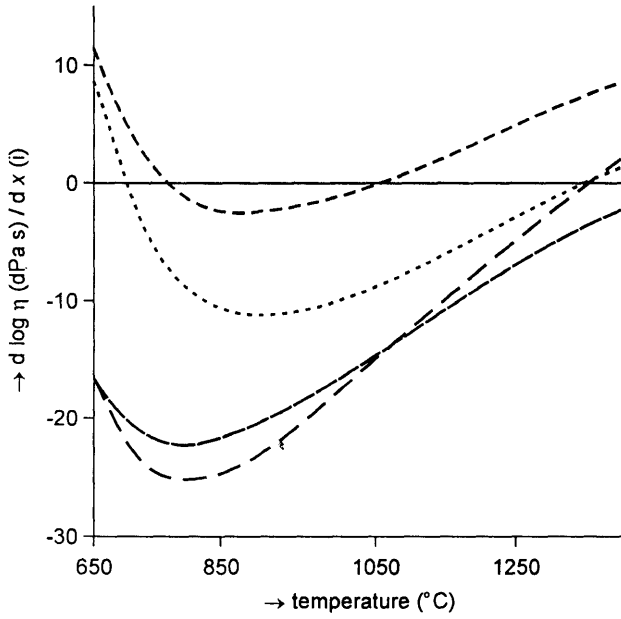
Figure 1. The temperature dependence of partial derivatives of log(η(dPa s)) with respect to the mole fractions of oxides used in the viscosity regression equations (6-8).
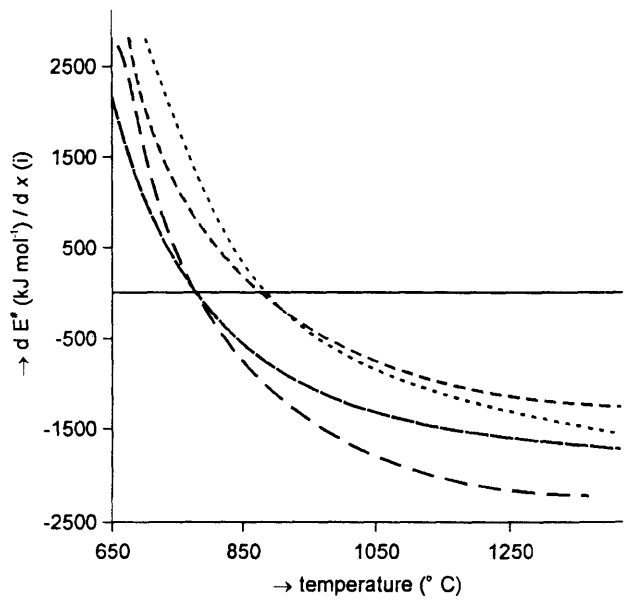

Figure 3. The temperature dependence of partial derivatives of viscous flow activation energy with respect to the mole fractions of oxides used in the viscosity regression equations (6-8).
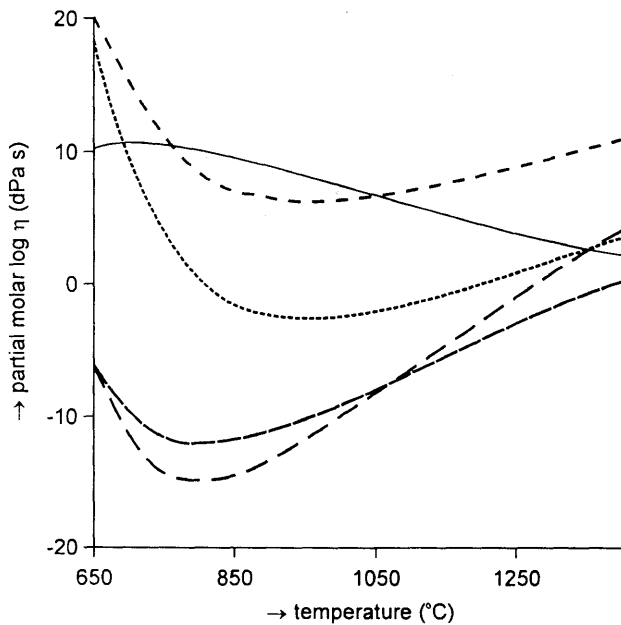

Figure 2. The temperature dependence of partial molar contributions of the individual oxides to log(η (dPa s)) value.
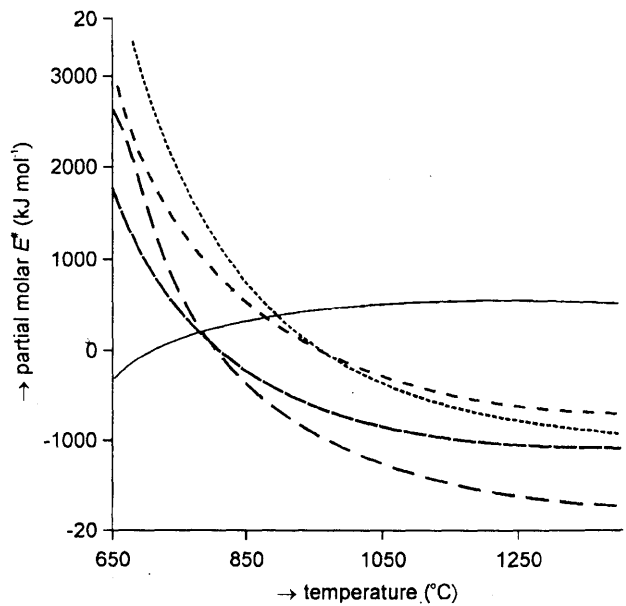

Figure 4. The temperature dependence of partial molar contributions of the individual oxides to the value of viscous flow activation energy.

commonly accepted network-modifying activity of these oxides. From this point of view, the near zero positive value of d_{T_g}(CaO) value seems to be unexpected.

Liquidus temperature

No theoretical qualitative predictions can be made about the individual oxides' influence on the liquidus temperature without the knowledge of the pertinent multi-

component phase diagram. Thus we can only summarize obtained numerical results. In contrary to the case of transformation temperature, zero influence on T_1 was calculated for the barium oxide. Negative d_{T1} values were found for the other modifying oxides fulfilling the relationship

$$d_{T1}(K_2O) << d_{T1}(Na_2O) < d_{T1}(CaO) < d_{T1}(BaO) = 0.$$

Table 4. The partial molar contributions V of individual oxides to various properties (see equation (13)), and the partial derivatives d of the approximations polynomials of these properties.

	T_g (°C)	T_1 (°C)	n_D	W_R (ml)
$V_y(CaO)$	817	-2619	1.6396	-28.3
$V_y(BaO)$	-2464	2352	1.5045	-45.1
$V_y(Na_2O)$	-254	-3551	1.5045	4.0
$V_y(K_2O)$	-1018	-8528	1.5045	4.0
$V_y(SiO_2)$	757	2352	1.5045	4.0
$d_y(CaO)$	61	-4970	0.1352	-32.3
$d_y(BaO)$	-3221	0	0	-49.1
$d_y(Na_2O)$	-1011	-5902	0	0
$d_y(K_2O)$	-1774	-10879	0	0

Table 5. The partial molar contributions V of individual oxides to the viscosity and viscous flow activation energy (see equation (13)), and the partial derivatives d of the approximations polynomials of these properties.

	$\log(\eta(dPa\ s))$ (700 °C)*	$\log(\eta(dPa\ s)$ (1000 °C)**	$E^*(kJ\ mol^{-1})$ (700 °C)***	$E^*(kJ\ mol^{-1})$ (1000 °C)****
$V_y(CaO)$	9.9	-2.6	2753	-176
$V_y(BaO)$	15.2	6.3	1987	-137
$V_y(Na_2O)$	-9.7	-9.1	990	-705
$V_y(K_2O)$	-11.6	-10.2	1473	-1117
$V_y(SiO_2)$	10.8	7.3	-54	480
$d_y(CaO)$	-0.9	-9.9	2808	-656
$d_y(BaO)$	4.4	-1.0	2042	-616
$d_y(Na_2O)$	-20.4	-16.4	1045	-1184
$d_y(K_2O)$	-22.4	-17.5	1528	-1597

*$\log(\eta_{700\ °C}(dPa\ s)) = 7.67$
**$\log(\eta_{1000\ °C}(dPa\ s)) = 4.05$
***E^* (700 °C) = 358 (kJ mol^{-1})
****E^*(1000 °C) =229 (kJ mol^{-1})

Refractive index

The small variance of refractive index experimental values caused that only the CaO/SiO_2 substitution was proved to be statistically significant with the positive $d_n(CaO)$ value. This is obviously an artifact caused by the narrow compositional range studied.

Hydrolytic resistance

The significant enhancement of hydrolytic resistance by the BaO/SiO_2 and CaO/SiO_2 substitution was confirmed by the highly negative values of $d_{WR}(BaO)$ and $d_{WR}(CaO)$. In the studied compositional region the effects of sodium and potassium oxides were completely statistically overwhelmed by the above influence.

Viscosity

The temperature dependencies of log η compositional derivatives d_η (i) and of the partial molar contributions V_η (i) of individual oxides i to log η values are plotted in figures 1 and 2. The strongest mutually comparable modifying activity of alkaline oxides resulted in significant negative values of d_η (Na_2O), d_η (K_2O), V_η (Na_2O), and V_η (K_2O). This alkaline oxides activity is most pronounced at temperatures about 750 - 850 °C. On the other hand, in the high temperature region, where the silicate network is highly thermally disrupted, the modifying effect of alkaline oxides is minimized, e.g. the respective d_η and V_η values are close to zero. Similar, but not so expressive, course of d_η and d_η V_η temperature dependencies may be found (figures 1 and 2) for alkaline earth oxides. The unexpected effect of increasing the viscosity value (i.e. positive d_η values) was found for low (below approx. 750 °C) and high (above approx. 1050 °C) temperature values in the case of BaO. Here the modifying activity of BaO is probably overwhelmed by its high molar weight. Finally, the positive values of V_η SiO_2) are in agreement with its network-forming function (figure 2).

The temperature and compositional dependencies of the viscous flow activation energy are illustrated in figures 3 and 4. Like in the above case of viscosity, the similar courses of the d_E and V_E curves for Na_2O and K_2O oxides on one side, and for CaO and BaO on the other, are observed. All the above oxides increase the slope of viscosity curve in low temperature region, while the negative value of d_E and V_E are observed in the high temperature region. Lower values of viscous flow activation energy are obtained for alkaline oxides than for alkaline earth oxides in the whole temperature range studied. This fact can be explained by the greater electrostatic field of alkaline earth cations, and by the greater modifying activity of alkaline oxides.

CONCLUSIONS

Compositional dependencies of studied properties of title glasses were described by equations (1-8) with sufficient accuracy for technological applications in the studied compositional range.

Using the above equations the new glass composition was proposed, that resulted in the batch cost lowering by about 9 %.

Some structural information was extracted from the statistically significant description of property--composition dependencies using mole fractions representation.

Ackowledgement

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VLASTNOSTI SKIEL V SÚSTAVE $Na_2O-K_2O-CaO-BaO-SiO_2$

PETER ŠIMURKA, MAREK LIŠKA*, JOZEF ANTALÍK**

LR CRYSTAL,
020 61 Lednické Rovne, Slovenská republika

*Ústav anorganickej chémie SAV,
M. Rázusa 10, 911 01 Trenčín, Slovenská republika
E-mail: liska@uach1.savba.sk

**Chemickotechnologická fakulta,
Slovenská Technická Univerzita,
Radlinského 9, 812 37 Bratislava, Slovenská republika

Experimentálne sa stanovili hodnoty teploty likvidus, teploty skelného prechodu, indexu lomu, odolnosti voči vode a teplotnej závislosti dynamickej viskozity (Tab. 2) pätnástich skiel (Tab. 1) zo sústavy $CaO-BaO-Na_2O-K_2O-SiO_2$. Nelineárnou regresnou analýzou sa určili optimálne tvary závislostí konštánt *A, B* a T_0 Vogelovej Fulcherovej Tammannovej viskozitnej rovnice (5) od zloženia vyjadrené v zmiešaných polynómoch (6-8) s nezávisle premennými mólovými zlomkami oxidov CaO, BaO, Na_2O a K_2O. Závislosť ostatných meraných fyzikálnych veličín od zloženia skla sa metódou lineárnych najmenších štvorcov opísala zmiešanými polynómami vyjadrenými ako v hmotnostných (1-4), tak aj v mólových zlomkoch (9-12) uvedených oxidov.

Na základe získaných výsledkov (vyjadrenie v hmotnostných percentách) sa optimalizovalo chemické zloženie bárnatého krištálového skla, pričom sa dosiahla 9 %-ná úspora v cene sklárskeho kmeňa.

Výsledky vyjadrené s použitím mólových zlomkov umožnili relatívne posúdenie modifikujúcej schopnosti použitých oxidov alkalických kovov a oxidov kovov alkalických zemín (Tab. 4, 5).

Práca je ilustráciou a metodickým návodom na súčasné využitie jediného súboru experimentálnych dát pri riešení technologických úloh a úloh základného výskumu v oblasti vzťahu medzi štruktúrou, zložením a vlastnosťami oxidových skiel.