J Therm Anal Calorim (2012) 109:831–840
DOI 10.1007/s10973-011-1740-1

Thermodynamic model and physical properties of selected zirconia containing silicate glasses

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Received: 2 May 2011 / Accepted: 10 June 2011 / Published online: 17 July 2011

Abstract The compositional dependence of density, molar volume, thermal expansion, glass transition temperature, refractive index, and molar refractivity of glasses with composition $x\mathrm{Na_2O}\cdot(15-x)\mathrm{K_2O}\cdot y\mathrm{CaO}\cdot(10-y)\mathrm{ZnO}\cdot z\mathrm{ZrO_2}\cdot(75-z)\mathrm{SiO_2}$ ($x = 0$, 7.5, 15; $y = 0$, 5, 10; $z = 0$, 1, 3, 5, 7) was analyzed. The studied glasses were described by the thermodynamic model of Shakhmatkin and Vedishcheva considering the glass as an equilibrium ideal solution of species with stoichiometry given by the composition of stable crystalline phases of respective glass forming system. Property–composition relationships were described by the regression approach considering the particular physical quantity as multilinear function of molar amounts of system components. The classical approach where the mole fractions of individual oxides are considered as independent variables was compared with the thermodynamic model. On the basis of statistical analysis there was proved that the thermodynamic model is able to describe the composition–property relationships with higher reliability. Moreover, due its better physical justification, thermodynamic model can be even used for predictive purposes.

Keywords Zirconia-silicate glasses · Thermodynamic model · Physical properties · Property–composition relationships

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Introduction

The physical properties of $x\mathrm{Na_2O}\cdot(15-x)\mathrm{K_2O}\cdot y\mathrm{CaO}\cdot(10-y)\mathrm{ZnO}\cdot z\mathrm{ZrO_2}\cdot(75-z)\mathrm{SiO_2}$ ($x = 0$, 7.5, 15; $y = 0$, 5, 10; $z = 0$, 1, 3, 5, 7) glasses and glass melts were studied in our previous work [1–5]. The reason for this study was the extraordinary importance of this glass system for glass technology, namely for Portland cement composites and for the replacement of toxic oxides (barium oxide, lead oxide) in crystal glass to minimize the impact of glass production on the environment, to minimize health hazards of the product, and to increase its dishwashing resistance [6–8]. The knowledge of the property–composition relationships is the compulsory prerequisite for targeted optimization of the glass composition. The standard treatment considering the particular property as a multilinear function of molar fractions of individual oxides often fails and needs an empirical addition of interaction terms represented by products and/or powers of independent variables. Therefore, the aim of this study resides in application of thermodynamic model of Shakhmatkin and Vedishcheva for property–composition multilinear regression.

Experimental part

The glass batches were prepared by mixing powdered carbonates and oxides. Glasses were melted in Pt-10% Rh crucible in superkanthal furnace at temperature of 1600 °C for 2–3 h 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 1 h at 650 °C, after which the furnace was switched off and samples allowed remain there until completely cool.

The chemical composition of studied glasses was determined after their decomposition by the mixture of HF and $HClO_4$ by inductively coupled plasma optical emission spectroscopy (VARIAN-Vista MPX/ICP-OES). The content of SiO_2 has not been analyzed. Chemical composition of studied silicate glasses is summarized in Table 1.

The densities of glasses at laboratory temperature were measured by Archimedes method by dual weighting in air and in distilled water. Thermal expansion and glass transition temperature were measured by thermodilatometry. Refractive index was measured on polished prismatic glass samples by Abbe's refractometer at 20 °C. Experimental details can be found in [1–5]. Obtained experimental data used for presented regression treatment are summarized in Table 2.

Thermodynamic model

Shakhmatkin and Vedishcheva proposed the thermodynamic model (TD) of glasses and glassforming melts [9–

Table 1 The composition and abbreviation of studied glasses (mol%) [1–3, 5]

Glass	Na_2O	K_2O	CaO	ZnO	ZrO_2	SiO_2
NCZ0	15.30	0	9.22	0	0	75.48
NCZ1	13.86	0	10.69	0	0.93	74.52
NCZ3	13.42	0	10.19	0	2.86	73.53
NCZ5	14.99	0	10.00	0	4.87	70.14
NCZ7	14.07	0	9.78	0	6.77	69.38
KCZ0	0	14.98	8.42	0	0	76.60
KCZ1	0	14.29	8.44	0	1.02	76.25
KCZ3	0	15.41	10.08	0	3.28	71.23
KCZ5	0	15.44	10.06	0	4.92	69.58
NzZ0	14.80	0	0	9.90	0	75.30
NzZ1	15.04	0	0	9.41	1.03	74.52
NzZ3	15.29	0	0	11.04	3.19	70.48
NzZ5	14.77	0	0	9.01	4.90	71.32
NzZ7	14.18	0	0	9.89	6.54	69.39
KzZ0	0	15.74	0	8.47	0	75.79
KzZ1	0	14.93	0	10.49	0.97	73.61
KzZ3	0	14.20	0	9.86	2.80	73.14
KzZ5	0	16.00	0	10.44	4.91	68.65
NKCZ1	7.64	7.36	8.61	0.00	0.95	75.44
NKzZ1	7.45	7.41	0.00	10.08	0.98	74.08
NCzZ1	13.51	0.00	4.80	4.58	0.89	76.22
KCzZ1	0.00	15.81	5.03	5.27	1.01	72.88
NKCzZ1	8.22	8.01	4.40	5.40	1.05	72.92
NKCZ3	7.54	7.44	8.84	0	2.86	73.32
NKzZ3	7.30	7.06	0	9.63	2.61	73.40
NCzZ3	13.72	0	4.72	5.01	2.71	73.84
KCzZ3	0	13.95	4.47	4.95	2.66	73.97
NKCzZ3	6.61	6.96	4.41	4.81	2.58	74.63
NKCZ5	7.74	6.89	9.97	0	5.12	70.28
NKzZ5	7.66	7.13	0	10.92	5.22	69.07
NCzZ5	15.78	0	5.13	5.58	5.42	68.09
KCzZ5	0	13.64	4.97	5.48	5.20	70.72
NKCzZ5	7.82	7.18	5.18	5.63	5.35	68.85
NKCZ7	7.66	7.01	9.98	0	7.18	68.17
NKzZ7	7.83	7.00	0	11.03	7.54	66.60
NCzZ7	15.78	0	5.11	5.43	7.40	66.29
KCzZ7	0	13.88	4.98	5.43	7.25	68.46
NKCzZ7	7.86	6.99	5.00	5.53	7.40	67.22

Table 2 Measured physical properties of studied glasses [1–3, 5]

Glass	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	n_D	R_m/cm^3 mol^{-1}	10^7 α_g/K^{-1}	10^7 α_m/K^{-1}	T_g/K
NCZ0	2.475	24.24	1.514	7.299	95.4	357	807
NCZ1	2.506	24.14	1.519	7.332	95.9	320	830
NCZ3	2.572	24.00	1.532	7.437	94.1	292	850
NCZ5	2.643	23.85	1.546	7.556	85.4	255	867
NCZ7	2.702	23.77	1.560	7.684	86.6	325	907
KCZ0	2.478	26.17	1.516	7.907	103	330	860
KCZ1	2.489	26.22	1.519	7.960	102	263	883
KCZ3	2.573	26.04	1.535	8.110	104	209	891
KCZ5	2.631	25.87	1.547	8.204	84.1	347	945
NzZ0	2.559	24.41	1.507	7.268	90.7	254	794
NzZ1	2.635	23.92	1.520	7.274	93.6	276	810
NzZ3	2.704	23.94	1.535	7.448	81.4	251	837
NzZ5	2.738	23.88	1.544	7.535	79.2	189	851
NzZ7	2.830	23.53	1.564	7.651	80.2	172	862
KzZ0	2.570	26.17	1.511	7.841	103	269	852
KzZ1	2.613	26.03	1.518	7.886	98.0	262	888
KzZ3	2.635	26.11	1.525	7.995	89.4	227	947
KzZ5	2.737	25.89	1.545	8.190	86.0	249	978
NKCZ1	2.505	25.15	1.519	7.636	106	345	835
NKzZ1	2.600	25.20	1.516	7.605	95.1	282	827
NCzZ1	2.558	24.12	1.518	7.312	74.4	291	801
KCzZ1	2.536	26.43	1.515	7.970	88.3	236	863
NKCzZ1	2.554	25.30	1.518	7.669	84.1	356	834
NKCZ3	2.571	24.98	1.530	7.715	100	279	850
NKzZ3	2.661	24.93	1.528	7.677	85.7	217	837
NCzZ3	2.628	23.95	1.532	7.422	79.5	281	832
KCzZ3	2.589	26.03	1.525	7.983	106	173	871
NKCzZ3	2.620	24.83	1.532	7.692	97.9	274	834
NKCZ5	2.655	24.64	1.548	7.829	97.4	269	883
NKzZ5	2.777	24.59	1.548	7.805	84.5	216	871
NCzZ5	2.750	23.56	1.556	7.574	90.5	269	855
KCzZ5	2.690	25.64	1.545	8.111	83.6	246	946
NKCzZ5	2.728	24.58	1.554	7.877	87.5	242	845
NKCZ7	2.726	24.49	1.564	7.963	81.4	275	905
NKzZ7	2.852	24.45	1.565	7.966	77.8	220	904
NCzZ7	2.812	23.47	1.569	7.692	76.7	258	877
KCzZ7	2.760	25.49	1.560	8.248	68.7	251	983
NKCzZ7	2.797	24.40	1.564	7.942	76.7	238	875

16] that could be considered as the extension of the Conrad's model [17, 18]. This model considers glasses and melts as a solution formed from salt-like products of interaction between the oxide components and from the original (unreacted) oxides. These salt-like products (also called associates, groupings, or species) have the same stoichiometry as the crystalline compounds, which exist in the equilibrium phase diagram of the system considered. The model does not use adjustable parameters; only the standard Gibbs energies of formation of crystalline compounds and the analytical composition of the system considered are used as input parameters. On the basis of the crystal structure of stable crystalline phases same information about the glass structure can be reached and compared with experimental results [19, 20].

The minimization of the systems Gibbs energy constrained by the overall system composition has to be performed with respect to the molar amount of each system

component to reach the equilibrium system composition [21]. The total Gibbs energy is expressed supposing the state of the ideal solution:

$$G(n_1, n_2 \ldots n_N) = \sum_{i=1}^{N} n_i \Delta_f G_{m,i} + RT \sum_{i=1}^{N} n_i \ln\left(n_i \Big/ \sum_{j=1}^{N} n_j \right), \quad (1)$$

where N is the number of components, n_i is the molar amount of ith component, T is the system temperature (i.e., the glass transition temperature, T_g, for particular glass) and $\Delta_f G_{m,i}$ is the molar Gibbs formation energy of pure ith component at the pressure of the system and temperature T. The system components are ordered such way that X_i ($i = 1, 2 \ldots M < N$) are pure oxides and X_i ($i = M + 1, M + 2 \ldots N$) are compounds formed from oxides by reversible reactions

$$X_i \leftrightarrow \sum_{j=1}^{M} v_{i,j} X_j, \quad i = M + 1, M + 2 \ldots N. \quad (2)$$

Let us suppose the system composition given by the molar amounts of pure unreacted oxides $n_{0,j}$ ($j = 1, 2 \ldots M$). Then the mass balance constraints can be written in the form:

$$n_{0,j} = n_j + \sum_{i=M+1}^{N} v_{i,j} n_i, \; j = 1, 2, \ldots M. \quad (3)$$

The molar Gibbs formation energies of the melts of pure components may be used in more advanced version of this model. However, these thermodynamic data are relatively scarce that prevents routine application of the model to the study of multicomponent systems. On the other hand, the errors caused by substituting the melt by the crystalline state are partially compensated when the reaction Gibbs energy, $\Delta_r G_{m,i}$ is calculated according:

$$\Delta_r G_{m,i} = \Delta_f G_{m,i} - \sum_{j=1}^{M} v_{i,j} \Delta_f G_{m,j} = -RT \ln K_i, \quad i = M + 1, M + 2 \ldots N, \quad (4)$$

where K_i is the equilibrium constant of the ith equilibrium reaction described by the Eq. 0.

In this study, the Na_2O–K_2O–CaO–ZnO–ZrO_2–SiO_2 six-component glass forming system is studied, thus $M = 6$. The glass is considered as an ideal solution of 52 species ($N = 52$) consisting of 6 oxides and 46 compounds formed by the reactions between oxides (see Table 3). Then, for example, the reaction Gibbs energy for the $Na_2Ca_3Si_6O_{16}$ formation from pure oxides is according to the Eq. 4 given by:

$$\Delta_r G_m(Na_2Ca_3Si_6O_{16}) = G_m(Na_2Ca_3Si_6O_{16}) - G_m(Na_2O) - 3G_m(CaO) - 6G_m(SiO_2), \quad (5)$$

Table 3 Stable crystalline phases considered in the Na_2O–K_2O–CaO–ZnO–ZrO_2–SiO_2 system [29]

Stoichiometry	No.	Abbrev.
Na_2O	–	Na2O
K_2O	–	K2O
CaO	–	CaO
ZnO	1	ZnO
ZrO_2	2	ZrO2
SiO_2	3	SiO2
Na_2SiO_3	4	NS
$Na_2Si_2O_5$	5	NS2
Na_4SiO_4	–	N2S
$Na_4CaSi_3O_9$	–	N2CS3
$Na_6Si_2O_5$	–	N3S2
$Na_6Si_8O_{19}$	–	N3S8
$Ca_3Si_2O_7$	6	C3S2
$Na_2Ca_3Si_6O_{16}$	7	NC3S6
$Na_2CaSi_5O_{12}$	8	NCS5
K_2SiO_3	–	KS
K_2SiO_4	9	KS2
$K_2Si_4O_9$	10	KS4
$CaSiO_3$	11	CS
Ca_2SiO_4	–	C2S
Ca_3SiO_5	–	C3S
$Na_2Ca_2Si_3O_9$	–	NC2S3
$Ca_2ZnSi_2O_7$	–	C2ZnS2
$CaZrO_3$	–	CZr
Zn_2SiO_4	12	Zn2S
$ZrSiO_4$	13	ZrS

Components with significant abundance in studied glasses are numbered

where the formation Gibbs energies, $\Delta_f G_{m,i}$, were substituted by molar Gibbs energies of pure substances, $G_{m,i}$, at the system temperature and pressure. Solving the thermodynamic model by constrained system Gibbs energy minimization is then equivalent to find the simultaneous equilibrium of 46 reactions of formation of the considered compounds from pure oxides.

When the crystalline state data are used the model can be simply applied to most multicomponent glasses including the non-oxide ones. Especially, the application of the model to the multicomponent industrially produced glasses can be very important. Taking into account that the common praxis resides in expressing most of the multicomponent glass properties in the form of (mostly) additive functions of the glass composition expressed in percents (even weight and not molar!) of pure oxides [22–24] using the thermodynamic model unambiguously represents the significant progress.

The contemporary databases of thermodynamic properties (like the FACT computer database [25]) enable the

Table 4 Equilibrium molar amounts n_i (given in 10^{-3} mol) of species with significant abundance in studied glasses

Glass	n_1	n_2	n_3	n_4	n_5	n_6	n_7	n_8	n_9	n_{10}	n_{11}	n_{12}	n_{13}
NCZ0	0	0	336	27	85	3	24	13	0	0	1	0	0
NCZ1	0	2	323	22	70	4	28	14	0	0	1	0	8
NCZ3	0	6	314	22	67	4	26	14	0	0	2	0	23
NCZ5	0	12	251	29	76	6	24	13	0	0	2	0	37
NCZ7	0	18	251	27	68	8	21	14	0	0	3	0	49
KCZ0	0	0	286	0	0	0	0	0	101	48	84	0	0
KCZ1	0	3	290	0	0	0	0	0	95	48	84	0	8
KCZ3	0	10	210	0	0	0	0	0	118	36	100	0	23
KCZ5	0	18	189	0	0	0	0	0	120	34	100	0	31
NzZ0	19	0	452	36	111	0	0	0	0	0	0	40	0
NzZ1	20	2	435	37	112	0	0	0	0	0	0	37	8
NzZ3	24	7	370	41	111	0	0	0	0	0	0	43	25
NzZ5	22	11	383	39	108	0	0	0	0	0	0	34	38
NzZ7	25	15	361	39	102	0	0	0	0	0	0	37	50
KzZ0	20	0	301	0	0	0	0	0	102	55	0	32	0
KzZ1	25	2	287	0	0	0	0	0	97	52	0	40	7
KzZ3	28	8	288	0	0	0	0	0	89	52	0	35	20
KzZ5	33	18	212	0	0	0	0	0	115	44	0	36	31
NKCZ1	0	2	281	11	32	3	24	7	46	28	1	0	8
NKzZ1	21	2	362	19	55	0	0	0	47	27	0	40	8
NCzZ1	12	1	416	27	85	2	11	10	0	0	1	17	7
KCzZ1	16	3	249	0	0	0	0	0	113	44	50	18	7
NKCzZ1	15	2	278	17	46	2	11	6	54	26	1	20	8
NKCZ3	0	6	250	11	30	4	24	7	49	25	2	0	22
NKzZ3	22	5	357	19	54	0	0	0	45	25	0	37	21
NCzZ3	14	5	375	28	85	2	10	11	0	0	1	18	22
KCzZ3	16	7	290	0	0	0	0	0	94	45	44	17	20
NKCzZ3	13	5	332	12	35	2	11	6	44	26	1	17	21
NKCZ5	0	14	210	11	27	6	26	6	48	21	3	0	38
NKzZ5	26	13	293	22	54	0	0	0	49	22	0	41	39
NCzZ5	17	13	267	39	93	4	11	9	0	0	1	20	41
KCzZ5	21	17	251	0	0	0	0	0	95	41	49	17	35
NKCzZ5	16	13	236	17	40	3	13	5	52	19	2	20	40
NKCZ7	0	22	187	12	26	8	24	6	51	19	4	0	50
NKzZ7	30	23	262	24	54	0	0	0	50	19	0	40	53
NCzZ7	18	21	244	41	91	5	10	9	0	0	2	18	53
KCzZ7	23	27	222	0	0	0	0	0	100	38	49	16	45
NKCzZ7	18	21	220	18	39	4	11	5	52	18	2	19	53

Species numbering is given in Table 3

routine construction of the Shakhmatkin and Vedishcheva model [16] for most of important multicomponent systems. It is worth noting that other methods of thermodynamic modeling of glasses and glassforming melts (not discussed here, e.g., [26–28]) do not posses the possibility of routine application to multicomponent systems.

Results and discussion

The 26 stable crystalline phases considered in the studied glass system are summarized in Table 3. For each glass composition the TD model was evaluated at the glass transition temperature. The system was created from 1 mol of individual oxides, i.e.,

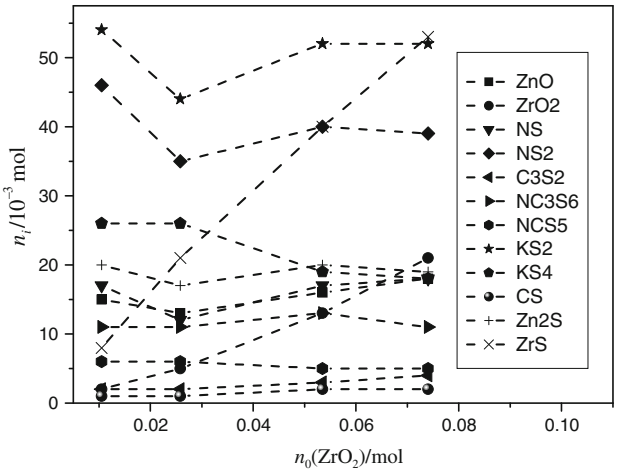

Fig. 1 Equilibrium molar amounts of individual components (with the exception of SiO_2) in NKCzZ*x* ($x \equiv 1, 3, 5, 7$) glasses (data taken from Table 4)

$$n_0(Na_2O) + n_0(K_2O) + n_0(CaO) + n_0(ZnO) + n_0(ZrO_2) + n_0(SiO_2) = 1 \text{ mol}. \quad (6)$$

Thirteen species with significant equilibrium abundance were found (see Table 3 where these components are numbered). Threshold of 0.01 mol of oxides obtained by decomposition of the species equilibrium amount was applied for qualification of significant species abundance. Equilibrium molar amounts of these species are summarized in Table 4. With the exception of SiO_2 the dependence of equilibrium molar amounts of significant components on $n_0(ZrO_2)$ given by the glass chemical analysis is plotted in Fig. 1 for the glass series NKCzZ*x*, where $x \equiv 1, 3, 5$, and 7.

The property–composition relationships were described by the multilinear equation:

$$p = a_0 + \sum_{i=1}^{13} a_i n_i, \quad (7)$$

Table 5 Results of multilinear regression analysis (Eqs. 7, 8), s_{appr} standard deviation of approximation, r correlation coefficient, F Fisher's F-statistics

Comp.	Value	ρ/g cm^{-3}	V_m/cm^3 mol^{-1}	n_D	R_m/cm^3 mol^{-1}
	a_0	2.724 ± 0.059	24.16 ± 0.16	1.512 ± 0.001	7.258 ± 0.009
ZnO	a_1	–	–	–	–
ZrO2	a_2	3.016 ± 0.945	−23.86 ± 4.28	0.740 ± 0.182	6.904 ± 1.549
SiO2	a_3	–	–	–	–
NS	a_4	6.534 ± 1.651	−27.58 ± 10.62	0.658 ± 0.242	–
NS2	a_5	−3.433 ± 0.954	9.18 ± 4.35	−0.199 ± 0.083	–
C3S2	a_6	−4.602 ± 2.201	–	–	–
NC3S6	a_7	3.734 ± 0.676	–	–	0.954 ± 0.323
NCS5	a_8	−2.349 ± 1.043	–	–	–
KS2	a_9	–	13.97 ± 1.83	–	3.563 ± 0.378
KS4	a_{10}	−3.040 ± 1.075	13.74 ± 4.33	–	4.571 ± 0.720
CS	a_{11}	−1.378 ± 0.129	–	–	0.811 ± 0.158
Zn2S	a_{12}	–	–	−0.073 ± 0.025	–
ZrS	a_{13}	2.924 ± 0.496	–	0.655 ± 0.093	5.293 ± 0.650
	s_{appr}	0.011	0.12	0.002	0.018
	r	0.995	0.993	0.993	0.998
	F	339	456	447	1482
–	b_0	2.455 ± 0.005	24.23 ± 0.04	1.509 ± 0.001	7.247 ± 0.008
Na_2O	b_1	0.159 ± 0.033	–	0.019 ± 0.007	–
K_2O	b_2	–	13.70 ± 0.29	–	4.059 ± 0.053
CaO	b_3	–	–	–	0.400 ± 0.081
ZnO	b_4	1.060 ± 0.048	–	–	–
ZrO_2	b_5	3.566 ± 0.082	−9.70 ± 0.73	0.730 ± 0.018	5.671 ± 0.132
	s_{appr}	0.012	0.11	0.003	0.020
	r	0.993	0.993	0.990	0.998
	F	844	1291	875	2389

Table 6 Results of multilinear regression analysis (Eqs. 7, 8), s_{appr} standard deviation of approximation, r correlation coefficient, F Fisher's F-statistics

Comp.	Value	$10^7\ \alpha_g/K^{-1}$	$10^7\ \alpha_m/K^{-1}$	T_g/K
	a_0	96 ± 2	184 ± 46	–
ZnO	a_1	−353 ± 94	−1971 ± 653	–
ZrO2	a_2	−648 ± 129	10470 ± 2197	6637 ± 940
SiO2	a_3	–	–	–
NS	a_4	–	3903 ± 1387	−15767 ± 1181
NS2	a_5	–	–	10596 ± 486
C3S2	a_6	–	–	4467 ± 2040
NC3S6	a_7	–	–	7884 ± 809
NCS5	a_8	–	6111 ± 1497	11529 ± 814
KS2	a_9	–	–	932 ± 286
KS4	a_{10}	210 ± 52	2521 ± 1057	11217 ± 427
CS	a_{11}	–	–	2642 ± 282
Zn2S	a_{12}	–	–	4613 ± 667
ZrS	a_{13}	–	−5424 ± 977	2255 ± 445
	s_{appr}	6	27	10
	r	0.807	0.852	1.000
	F	21	14	24931
–	b_0	98 ± 3	279 ± 18	866 ± 7
Na_2O	b_1	–	–	−503 ± 60
K_2O	b_2	39 ± 18	–	–
CaO	b_3	–	644 ± 220	–
ZnO	b_4	−71 ± 27	–	–
ZrO_2	b_5	−226 ± 45	−1078 ± 358	1204 ± 147
	s_{appr}	7	54	22
	r	0.738	0.569	0.884
	F	14	8	62

where p stands for room temperature glass density (ρ) and molar volume (V_m), thermal expansion of glass (α_g) and metastable melt (α_m), glass transition temperature (T_g), refractive index at 20 °C (n_D), and molar refractivity (R_m), respectively.

Multilinear regression analysis was used for obtaining of estimates of the a_i parameters together with their standard deviations. By starting from the full Eq. 7 the statistically non-significant terms were rejected in a stepwise manner. The statistical significance of a_i ($i = 0, 1\ldots13$) estimates was determined on the basis of the Student's t-statistics at 95% significance level. The overall statistical quality of regression equation was characterized by standard deviation of approximation s_{appr} and by the value of Fisher's statistics. The obtained results are summarized in Tables 5 and 6.

For comparison, the analogous multilinear regression treatment of experimental data was applied by using the molar amounts of individual oxides (constrained by the Eq. 6 and hence numerically equal to mole fractions) as independent variables:

$$p = b_0 + \sum_{i=1}^{5} b_i n_{0,i} = b_0 + b_1 n_0(\mathrm{Na_2O}) + b_2 n_0(\mathrm{K_2O}) + b_3 n_0(\mathrm{CaO}) + b_4 n_0(\mathrm{ZnO}) + b_5 n_0(\mathrm{ZrO_2}). \quad (8)$$

This "pure oxides model" represents the common way of property–composition dependence description used in the glass science and technology [24]. The obtained results are summarized, together with the results of thermodynamic model, in Tables 5 and 6.

Comparing the regression results obtained by both models one can see that the values of standard deviation of approximation, s_{appr}, are close for most properties with the exception of the glass transition temperature and coefficient of thermal expansion of metastable melt, where the s_{appr} values for thermodynamic model are significantly lower. Comparing the values of correlation coefficient, r,

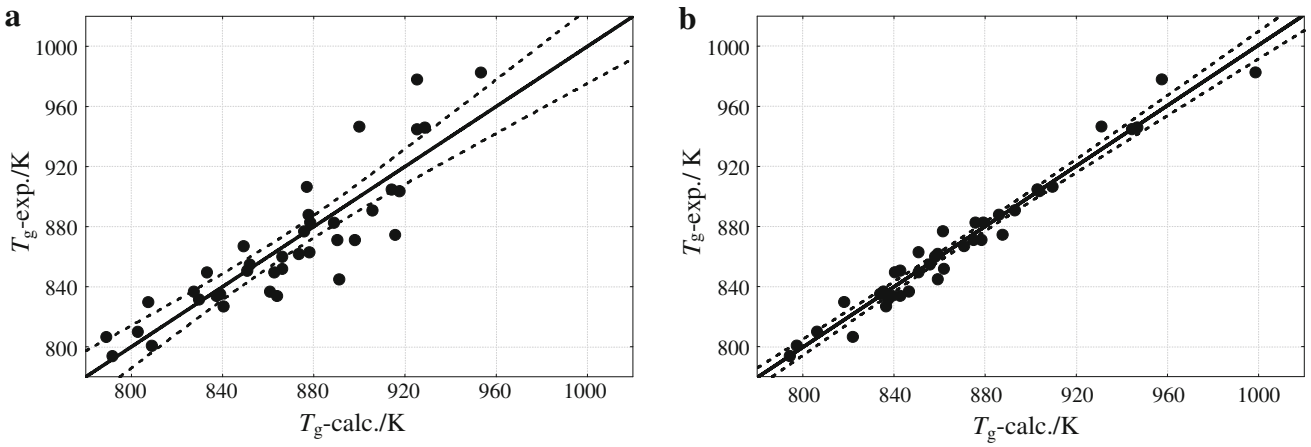

Fig. 2 Experimental versus calculated T_g values obtained by multilinear regression analysis according to the Eq. 8 (**a**) and by the thermodynamic model Eq. 7 (**b**). *Dotted lines* represent the 95% confidence limit

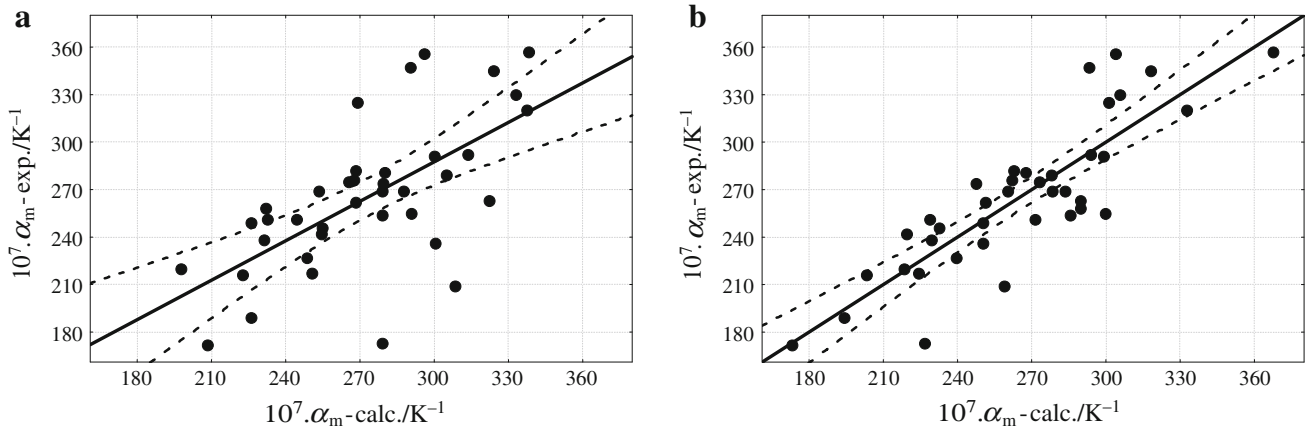

Fig. 3 Experimental versus calculated α_m values obtained by multilinear regression analysis according to the Eq. 8 (**a**) and by the thermodynamic model Eq. 7 (**b**). *Dotted lines* represent the 95% confidence limit

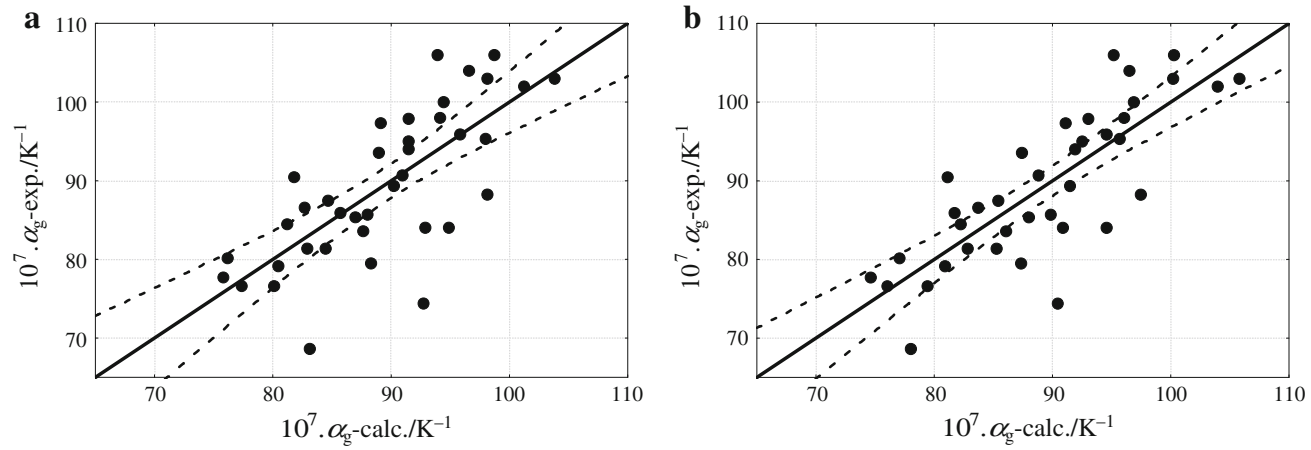

Fig. 4 Experimental versus calculated α_g values obtained by multilinear regression analysis according to the Eq. 8 (**a**) and by the thermodynamic model Eq. 7 (**b**). *Dotted lines* represent the 95% confidence limit

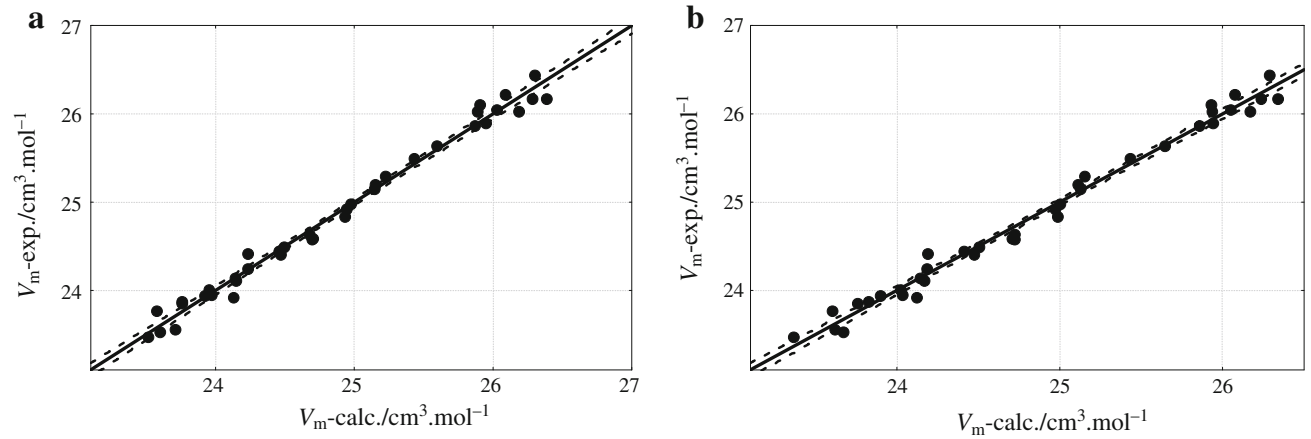

Fig. 5 Experimental versus calculated V_m values obtained by multilinear regression analysis according to the Eq. 8 (**a**) and by the thermodynamic model Eq. 7 (**b**). *Dotted lines* represent the 95% confidence limit

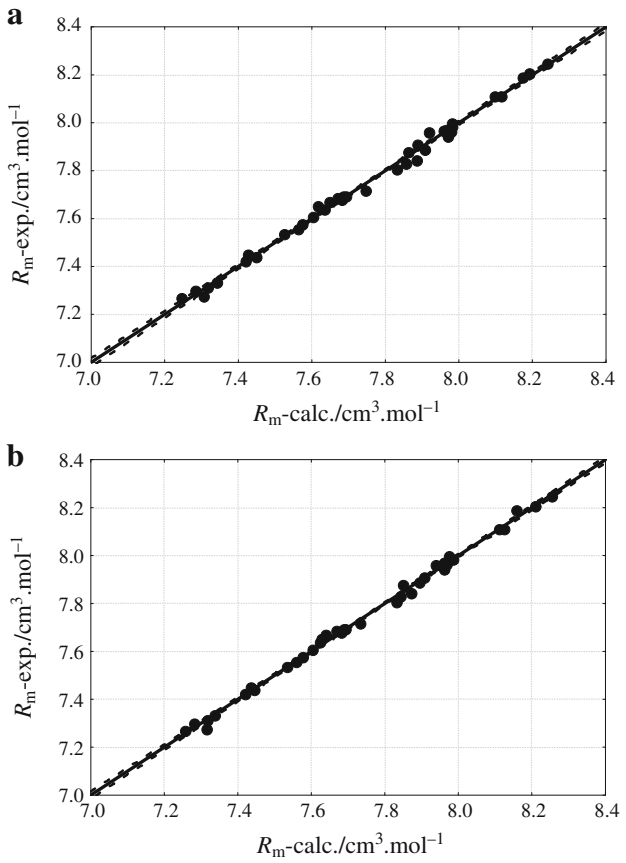

Fig. 6 Experimental versus calculated R_m values obtained by multilinear regression analysis according to the Eq. 8 (**a**) and by the thermodynamic model Eq. 7 (**b**). *Dotted lines* represent the 95% confidence limit

the values close to one are found for both considered models with the exception of α_g and α_m regressions, especially for the oxide model, and T_g regression for the oxide model. The values of Fisher's F-statistics are higher in the case of oxide model for "low temperature properties", i.e., for ρ, V_m, n_D, and R_m. However, in case of "higher temperature properties", especially for α_m, and T_g, the thermodynamic model gives much better description of experimental data. For the case of the glass transition temperature, glass and metastable equilibrium melt thermal expansion coefficient, molar volume, and molar refraction the graphical comparison of both fits is presented in Figs. 2, 3, 4, 5, and 6.

Conclusions

The thermodynamic model of studied Na_2O–K_2O–CaO–ZnO–ZrO_2–SiO_2 glasses revealed 13 components with significant equilibrium abundance at the T_g temperature. The compositional dependence of studied glass properties was successfully described in frame of the Shakhmatkin and Vedishcheva thermodynamic model by multilinear regression function of equilibrium molar amounts of significant components. However, only for the properties measured at higher temperature (thermal expansion coefficients and glass transition temperature) the results obtained by using the thermodynamic model were significantly better than those obtained by the common approach based on the mole fractions of pure oxides.

Acknowledgements This study was supported by Agency for Promotion Research and Development under the contract SUSPP-0006-09, by the Slovak Grant Agency for Science under the grant VEGA 1/0330/09. This publication was created in the frame of the project PVTECHSKLO, ITMS code 26220220072, of the Operational Program Research and Development funded from the European Fund of Regional Development.

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