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Thermal properties and thermodynamic model of lithium doped 45S5 bioglass

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Abstract
Shakhmatkin and Vedishcheva thermodynamic model (SV TDM) of the 45S5 Bioglass® doped with three different amounts of Li_2O (4.1, 9.9, and 12.3 mol%) was evaluated at T = 800 K. The 55 components of SV TDM were considered, among them 12 lithium containing compounds. Different number of components with not negligible equilibrium molar amount was found for different glass compositions (9 or 10). In all glass compositions containing nonzero amount of Li_2O, the four lithium compounds with not negligible equilibrium amount were identified, i.e., $Li_2O{\cdot}SiO_2$, $3Li_2O{\cdot}P_2O_5$, $Li_2O{\cdot}2CaO{\cdot}2SiO_2$, and $2Li_2O{\cdot}SiO_2$. In the 45S5 glass composition four phosphate compounds with not negligible abundance were identified: $9Na_2O{\cdot}6SiO_2{\cdot}2P_2O_5$, $Na_2O{\cdot}2CaO{\cdot}P_2O_5$, $5Na_2O{\cdot}4SiO_2{\cdot}P_2O_5$, and $Na_2O{\cdot}CaO{\cdot}P_2O_5$. In all other glasses the $3Li_2O.P_2O_5$ was found with not negligible abundance. Moreover, in the glass with 4.1 mol% Li_2O the $Na_2O{\cdot}2CaO{\cdot}P_2O_5$ and $3Li_2O{\cdot}P_2O_5$ compounds were found with not negligible abundance. For each studied glass the glass transition temperature, coefficient of thermal expansion of glass and metastable melt were measured by thermodilatometry. The low temperature viscosity was measured by thermomechanical analysis. The viscous flow activation energy was evaluated from the viscosity temperature dependence. The compositional dependence of measured thermal properties was analyzed by correlation analysis with the Q-distribution of silicate and phosphate units.

Keywords 45S5 bioglass · Li_2O · Thermodynamic model · TMA

Introduction

One of the most successful glassy materials in the field of biomedicine is the Bioglass® denoted 45S5. This glass has the following composition: 45 mass% SiO_2 (hence the denotation "45S"), 24.5 mass% CaO, 24.5 mass% Na_2O and 6 mass% P_2O_5. The high Ca:P ratio favor's the formation of apatite crystals, where the silicon and calcium atoms can act as crystallization centers. At the same time, this ratio (which is close to that of the actual bone matter) ensures that the human body will accept this artificial material without a negative immune response. Typical utilization of the Bioglass® 45S5 involves bone transplants, maxillofacial, and dental replacements, or stimulation of vessel/nerve regeneration [1–6]. The functionality of the Bioglass® particles is based on the formation of the surface coat of silica gel supporting (at contact with the body fluid) the adhesion of PO_4^{3-}, CO_3^{2-} and Ca^{2+} ions, creating a porous layer of hydroxyapatite. Such surface is then colonized by the stem cells, producing osteocytes and osteoblasts. The osteoblasts then secrete mineral precursors (calcium and phosphate rich structures containing organic material, such as acidic proteins) that consequently form the bone tissue [4–10]. The Bioglass® can be doped by large variety of elements, influencing its bioactivity, mechanical and biological response:

Zn—antibacterial, antifungal and anti-inflammatory effects [11–13];

Sr—supports bone regeneration [14, 15];

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Table 1 Composition of the studied Li-doped bioactive glasses and the 45S5 Bioglass® in mol%

Oxide	Glass abbreviation			
	Li0	Li1	Li2	Li3
SiO_2	47.5	45.6	43.9	41.8
CaO	27.6	26.3	25.2	23.8
Na_2O	22.3	21.9	19.8	20.0
P_2O_5	2.6	2.1	1.2	2.0
Li_2O	0.0	4.1	9.9	12.3

Ce—exhibits anti-inflammatory and antibacterial properties and supports osteogenesis (bone development) [16–19];

Ga—promotes osteogenesis and exhibits antibacterial activity [20, 21].

One of the very important dopants are the Li^+ ions. Substitution of the sodium ions by the lithium ones has markedly positive effect on the growth rate of the cell cultures, as well as on the activity of the alkaline phosphatase [22, 23]. Formation of the higher density bone tissue was reported [24–26] because of the cultivation on the Li-doped the Bioglass®. Similarly, positive influence of Li-incorporation on the bioactivity of the 45S5 Bioglass® was reported in [27, 28]. The confirmation of the enhanced bioactivity of the Li-doped the Bioglass® is, however, only half the picture needed for the successful application of these materials. The physico-chemical properties of the glasses are just as important, as they determine their workability, long-term stability, and processing conditions. Surprisingly, no available literature sources on the glass transition kinetics and the structural relaxation phenomena in the Li-doped the Bioglass® 45S5 have been found by the authors. Therefore, this work is aimed to investigate the above-mentioned features of the Li-doped bioactive glasses. In the work of the authors Khorami et al. [27] reported the incorporation of Li^+ into bioactive glasses, who focused on the modification of Na_2O with different amounts of Li_2O (3, 7 and 12 wt%) in the Bioglass® 45S5 glass system. Many other studies focused on investigating the effect of adding Li^+ to various biomaterials to investigate the osteogenic potential [26–31], but not on the evaluation of physicochemical and structural properties.

When studying the relationships between the structure, composition and properties of glasses, the method of thermodynamic modeling is intensively used, e.g. Conrad et al., Liška et al., Vedishcheva et al., Pedone et al., Bhaskar et al. [32–37].

This work deals with the application of the Shakhmatkin and Vedishcheva thermodynamic model (SV TDM) for the 45S5 Bioglass® doped with three different amounts of Li_2O (4.1, 9.9, and 12.3 mol%). SV TDM was evaluated at $T = 800$ K roughly corresponding to the glass transition temperature (T_g). For each studied glass the glass transition temperature, coefficient of thermal expansion of glass (α_g) and metastable melt (α_m) were measured by thermodilatometry. The low temperature viscosity was measured by thermomechanical analysis. The activation energy of the viscous flow was evaluated from the measured temperature dependence of viscosity. The compositional dependence of the measured thermal properties was analyzed using correlation analysis with the Q-distribution of silicate and phosphate units.

Experimental part

The 45S5 Bioglass® and doped the bioactive glass were prepared by mixing raw materials of analytical purity (≥ 99%): SiO_2 (Centralchem, Slovakia), $CaCO_3$ (Centralchem, Slovakia) Na_2CO_3 (Penta, Czech Republic), Li_2CO_3 (Penta, Czech Republic), and $Na_5P_3O_{10}$ (Sigma-Aldrich, Slovakia) and subsequent homogenization for 6 h.

The mixture was then melted in an ambient atmosphere in a Pt-10% Rh crucible in a superkanthal furnace at temperatures in the range of 1300–1400 °C for two hours. During melting, sufficient homogeneity of the melt was ensured by manually stirring. After the melt was clarified, the melting process ended and the clear glass was poured onto a stainless plate, which was then placed in a cooling furnace. The cooling process consisted of tempering at a temperature of 550 °C for 30 min and controlled cooling at 5 °C/min. to laboratory temperature.

The amorphous nature of the glasses was confirmed using the X-ray diffractometer Panalytical Empyrean DY1098—XRD.

The chemical composition of the prepared glasses was determined by the XRF analyzer S8 Tiger (Bruker). The glasses were ground in an agate ball mill to a powder with a

Table 2 Measured thermal properties of studied glasses

	$10^6\alpha_g/°C^{-1}$	$10^6\alpha_m/°C^{-1}$	T_g/°C	A	B/K	$s_{apr}/\log(\eta/dPa\ s^{-1})$	$E_{\eta*}$/kJ mol^{-1}
Li0	15.92 ± 0.02	44.68 ± 0.39	475 ± 0.8	− 27.6 ± 1.1	32 222 ± 980	0.12	617 ± 19
Li1	13.29 ± 0.01	52.07 ± 0.42	402 ± 0.9	− 27.9 ± 1.3	28 913 ± 986	0.15	554 ± 19
Li2	14.46 ± 0.01	48.23 ± 0.37	450 ± 1.0	− 26.3 ± 1.1	29 661 ± 938	0.12	568 ± 18
Li3	15.81 ± 0.02	46.41 ± 0.45	407 ± 0.9	− 26.8 ± 0.7	28 205 ± 521	0.06	540 ± 10

Table 3 Input data of SV TDM (considered components, their Q-units, and molar Gibbs energies G_m)

No	Abbr	Formula	$-G_m$/MJ mol^{-1}	Q^n
1	N	Na_2O	0.5034	–
2	C	CaO	0.6078	–
3	P	P_2O_5	1.6457	$2Q^3_P$
4	Si	SiO_2	0.9671	Q^4_{Si}
5	Li	Li_2O	6.4775	–
6	NS2	$Na_2O{\cdot}2SiO_2$	2.6698	$2Q^3_{Si}$
7	NS	$Na_2O{\cdot}SiO_2$	1.6985	Q^2_{Si}
8	N3S2	$3Na_2O{\cdot}2SiO_2$	4.0146	$2\,Q^1_{Si}$
9	N2S	$2Na_2O{\cdot}SiO_2$	2.3218	Q^0_{Si}
10	N3S8	$3Na_2O{\cdot}8SiO_2$	9.8947	$2\,Q^4_{Si}+6\,Q^3_{Si}$
11	N5S	$5Na_2O{\cdot}SiO_2$	3.7828	Q^0_{Si}
12	C2S	$2CaO{\cdot}SiO_2$	2.4449	Q^0_{Si}
13	C3S2	$3CaO{\cdot}2SiO_2$	4.1846	$2\,Q^1_{Si}$
14	CS	$CaO{\cdot}SiO_2$	1.7375	Q^2_{Si}
15	C3S	$3CaO{\cdot}SiO_2$	3.1089	Q^0_{Si}
16	CS2	$CaO{\cdot}2SiO_2$	2.7098	$2Q^3_{Si}$
17	NP	$Na_2O{\cdot}P_2O_5$	2.6907	$2\,Q^2_P$
18	N5P3	$5Na_2O{\cdot}3P_2O_5$	9.8017	$2\,Q^2_P+4\,Q^1_P$
19	N2P	$2Na_2O{\cdot}P_2O_5$	3.5520	$2\,Q^1_P$
20	N3P	$3Na_2O{\cdot}P_2O_5$	4.2283	$2\,Q^0_P$
21	CP	$CaO{\cdot}P_2O_5$	2.6754	$2\,Q^2_P$
22	C2P	$2CaO{\cdot}P_2O_5$	3.5517	$2\,Q^1_P$
23	C3P	$3CaO{\cdot}P_2O_5$	4.3811	$2\,Q^0_P$
24	C2P3	$2CaO{\cdot}3P_2O_5$	6.9744	$2\,Q^3_P+4\,Q^2_P$
25	C4P	$4CaO{\cdot}P_2O_5$	5.0608	$2\,Q^0_P$
26	C4P3	$4CaO{\cdot}3P_2O_5$	8.8234	$4\,Q^2_P+2\,Q^1_P$
27	CP2	$CaO{\cdot}2P_2O_5$	4.3396	$2\,Q^3_P+2\,Q^2_P$
28	PS	$P_2O_5{\cdot}SiO_2$	2.6762	$Q^4_{Si}+2\,Q^3_P$
29	P2S3	$2P_2O_5{\cdot}3SiO_2$	6.3038	$3\,Q^4_{Si}+4\,Q^3_P$
30	NC2S2	$Na_2O{\cdot}2CaO{\cdot}2SiO_2$	4.1211	Q^1_{Si}
31	NC3S3	$Na_2O{\cdot}3CaO{\cdot}3SiO_2$	5.2135	$3\,Q^2_{Si}$
32	NC3S6	$Na_2O{\cdot}3CaO{\cdot}6SiO_2$	8.9239	$4\,Q^3_{Si}+2\,Q^2_{Si}$
33	NCS5	$Na_2O{\cdot}CaO{\cdot}5SiO_2$	6.3490	$Q^4_{Si}+4\,Q^3_{Si}$
34	N2CS3	$2Na_2O{\cdot}CaO{\cdot}3SiO_2$	5.1228	$3Q^2_{Si}$
35	N4C3S5	$4Na_2O{\cdot}3CaO{\cdot}5SiO_2$	9.9194	$Q^2_{Si}+4\,Q^1_{Si}$
36	NC2P	$Na_2O{\cdot}2CaO{\cdot}P_2O_5$	4.3670	Q^0_P
37	NCP	$Na_2O{\cdot}CaO{\cdot}P_2O_5$	3.6222	$2\,Q^1_P$
38	N2CP3	$2Na_2O.CaO{\cdot}3P_2O_5$	8.1580	$6\,Q^2_P$
39	NC2P3	$Na_2O{\cdot}2CaO{\cdot}3P_2O_5$	8.1180	$6\,Q^2_P$
40	N9S6P2	$9Na_2O{\cdot}6SiO2{\cdot}2P_2O_5$	16.6773	$6\,Q^2_{Si}+4\,Q^0_P$
41	N5S4P	$5Na_2O{\cdot}4SiO2{\cdot}P_2O_5$	9.6782	$4\,Q^2_{Si}+2\,Q^2_P$
42	C5PS	$5CaO{\cdot}P_2O_5{\cdot}SiO_2$	6.8100	$Q^0_{Si}+2\,Q^0_P$
43	C7PS2	$7CaO{\cdot}P_2O_5{\cdot}2SiO_2$	9.2518	$2\,Q^0_{Si}+2\,Q^0_P$
44	LC2S2	$Li_2O{\cdot}2CaO{\cdot}2SiO_2$	4.2064	$2\,Q^1_{Si}$
45	LC3S6	$Li_2O{\cdot}3CaO{\cdot}6SiO_2$	8.8554	$2\,Q^2_{Si}+4\,Q^3_{Si}$
46	LC4S4	$Li_2O{\cdot}4CaO{\cdot}4SiO_2$	7.6601	$4Q^1_{Si}$
47	LCS	$Li_2O{\cdot}CaO{\cdot}SiO_2$	2.4002	Q^0_{Si}
48	L2S	$2Li_2O{\cdot}SiO_2$	2.4735	Q^0_{Si}
49	LS2	$Li_2O{\cdot}2SiO_2$	2.7122	$2\,Q^3_{Si}$
50	LS	$Li_2O{\cdot}SiO_2$	1.7483	Q^2_{Si}
51	L3NS2	$3Li_2O{\cdot}Na_2O{\cdot}2SiO_2$	4.8667	$2\,Q^0_{Si}$
52	L3P	$3Li_2O{\cdot}P_2O_5$	4.4911	$2\,Q^0_P$
53	L2P	$2Li_2O{\cdot}P_2O_5$	3.6169	$2\,Q^1_P$
54	L5P3	$5Li_2O{\cdot}P_2O_5$	9.8668	$4\,Q^1_P+2\,Q^2_P$
55	LP	$Li_2O{\cdot}P_2O_5$	2.6853	$2\,Q^2_P$

size fraction below 45 µm. Table 1 shows the experimental composition of studied glasses in mole percentages.

The glass transition was investigated using thermomechanical analysis using TMA Q EM 402 (TA Instrument) [38]. Prismatic samples were prepared by cutting and grinding to a size of 20 × 5 × 5 mm. Dilatometric curves were measured at a heating and cooling rate of 5 °C min^{-1} at a sample load of 5 g. Low-temperature viscosity between 10^8 dPa.s and 10^{12} dPa.s was measured by a thermomechanical analyzer (Netzsch, TMA 402) [38].

Shakhmatkin and Vedishcheva proposed a thermodynamic model that was successfully applied to the study of silicate and phosphate glasses [39, 40]. According to this model glasses and melts are ideal solutions formed from products of equilibrium chemical reactions between oxides and from the original un-reacted oxides. The input data for construction of SV TDM consists of the molar Gibbs energies of pure crystalline compounds at particular temperature, and the analytical composition of the particular system. The equilibrium molar amount of each of the systems species is obtained by minimization of the system's Gibbs energy constrained by the overall system composition [41]. It was verified that SV TDM can be used for most multicomponent glasses using the crystalline state data. The available databases of thermodynamic data (e.g. FACT [37, 42]) enable the simple construction of the SV TDM for various multicomponent systems. This approach enabled a direct connection between the glass structure and the balanced representation of individual glass components.

Results and discussion

The temperature dependence of measured viscosity was described by the Andrade's equation [43, 44]:

$$\log \eta = A + \frac{B}{T} \tag{1}$$

Table 4 Components of SV TDM with not negligible equilibrium molar amount (for each glass composition the components are ordered with decreasing molar amount n_{ox})

Li3		Li2		Li1		Li0	
component	n_{ox}/mol	component	n_{ox}/mol	component	n_{ox}/mol	component	n_{ox}/mol
NS	0.3852	NS	0.3776	NS	0.3384	NC3S6	0.3564
C3S2	0.1181	C3S2	0.1278	NC3S6	0.2010	NS	0.2550
LC2S2	0.1138	LC2S2	0.1090	CS	0.1132	CS	0.1011
C2S	0.0956	CS	0.1069	C3S2	0.1117	C3S2	0.0894
CS	0.0912	C2S	0.0876	C2S	0.0633	N9S6P2	0.0686
L3P	0.0758	LS	0.0775	NC2P	0.0340	NC2P	0.0525
LS	0.0747	L3P	0.0449	LC2S2	0.0323	C2S	0.0463
NC3S6	0.0110	NC3S6	0.0403	LS	0.0278	N5S4P	0.0114
NC2S2	0.0108	NC2S2	0.0107	L3P	0.0274	NCP	0.0104
L2S	0.0103			N9S6P2	0.0246		

Table 5 Si Q-distribution and P Q-distribution of SV TDM

	Si Q-distribution/%					P Q-distribution/%			
	Q^0	Q^1	Q^2	Q^3	Q^4	Q^0	Q^1	Q^2	Q^3
Li0	3.26	8.00	53.47	35.24	0.02	83.39	12.24	4.36	0
Li1	4.71	13.49	62.11	19.67	0.02	88.62	8.14	3.25	0
Li2	7.23	22.91	66.09	3.76	0.01	99.08	0.73	0.18	0
Li3	8.47	23.79	66.62	1.11	0.01	99.42	0.49	0.10	0

Table 6 Correlation coefficients between Li_2O content and relative amounts of Si Q-units and P Q-units

	Li_2O	SiQ^0	SiQ^1	SiQ^2	SiQ^3	SiQ^4	PQ^0	PQ^1	PQ^2
Li_2O	1.00	1.00	0.99	0.94	−0.99	−0.97	0.99	−0.99	−0.98
SiQ^0	1.00	1.00	0.98	0.92	−0.98	−0.99	0.98	−0.98	−0.98
SiQ^1	0.99	0.98	1.00	0.95	−0.99	−0.96	1.00	−1.00	−1.00
SiQ^2	0.94	0.92	0.95	1.00	−0.98	−0.84	0.94	−0.95	−0.92
SiQ^3	−0.99	−0.98	−0.99	−0.98	1.00	0.93	−0.99	0.99	0.98
SiQ^4	−0.97	−0.99	−0.96	−0.84	0.93	1.00	−0.95	0.95	0.96
PQ^0	0.99	0.98	1.00	0.94	−0.99	−0.95	1.00	−1.00	−1.00
PQ^1	−0.99	−0.98	−1.00	−0.95	0.99	0.95	−1.00	1.00	1.00
PQ^2	−0.98	−0.98	−1.00	−0.92	0.98	0.96	−1.00	1.00	1.00

Table 7 The correlation analysis between the measured properties an Si Q-distribution and P Q-distribution

	SiQ^0	SiQ^1	SiQ^2	SiQ^3	SiQ^4	PQ^0	PQ^1	PQ^2
$10^6\alpha_g$ [°C^{-1}]	0.11	0.00	−0.28	0.09	−0.28	0.01	0.01	−0.07
$10^6\alpha_m$ [°C^{-1}]	0.01	0.09	0.39	−0.19	0.16	0.07	−0.09	−0.01
T_g [°C]	−0.47	−0.43	−0.64	0.52	0.36	−0.39	0.41	0.35
E_{η^*} [kJ.mol^{-1}]	−0.77	−0.76	−0.90	0.82	0.67	−0.73	0.75	0.69

where A, and B are constants routinely determined by the regression analysis, and T is thermodynamic temperature. The activation energy of viscous flow, E_{η^*}, is given by the relation:

$$B = \frac{E_\eta^*}{2.303R} \tag{2}$$

where R is the molar gas constant. The Table 2 summarizes the values of A and B calculated by fitting Eq. (1), and the values of activation energy calculated using Eq. (2). The linear thermal expansion coefficients of glass, α_g, and metastable melt, α_m, were estimated from the slope of the cooling curve in temperature ranges of 300–350 and 450–550 °C, respectively. The glass transition temperatures, T_g, were determined from the intersection of two lines with slopes of α_g and α_m.

The 55 components of SV TDM were considered (Table 3), among them 12 lithium containing compounds. The significant (not negligible) abundance of system components was defined by the equilibrium molar amount reaching at least 0.01 mol of oxides, i.e. $n_{ox,i} \geq 0.01$ mol. When the stoichiometry of the ith component (X_i) is expressed by the reaction:

$$X_i = \rho_i * Li_2O + \nu_i * Na_2O + \mu_i * CaO + \lambda_i * SiO_2 + \sigma_i * P_2O_5 \quad (3)$$

then $n_{ox,i}$ is defined by:

$$n_{ox,i} = n_i * (\rho_i + \nu_i + \mu_i + \lambda_i + \sigma_i) \quad (4)$$

where n_i is the equilibrium molar amount of the ith component. Different number of components with not negligible equilibrium molar amount was found for different glass compositions (9 or 10), see Table 4. In all glass compositions containing nonzero amount of Li_2O, the four lithium compounds with not negligible equilibrium amount were identified, i.e. $Li_2O{\cdot}SiO_2$, $3Li_2O{\cdot}P_2O_5$, $Li_2O{\cdot}2CaO{\cdot}2SiO_2$, and $2Li_2O{\cdot}SiO_2$. In the 45S5 glass composition four phosphate compounds with not negligible abundance were identified: $9Na_2O{\cdot}6SiO_2{\cdot}2P_2O_5$, $Na_2O{\cdot}2CaO{\cdot}P_2O_5$, $5Na_2O{\cdot}4SiO_2{\cdot}P_2O_5$, and $Na_2O{\cdot}CaO{\cdot}P_2O_5$. In all other glasses the $3Li_2O{\cdot}P_2O_5$ was found with not negligible abundance. Moreover, in the glass with 4.1 mol% Li_2O the $Na_2O{\cdot}2CaO{\cdot}P_2O_5$ and $3Li_2O{\cdot}P_2O_5$ compounds were found with not negligible abundance.

Due to volatility of glass components during glass melting the analyzed glass composition strongly differs from the prescribed one. Due to this fact no straightforward dependence of measured quantities on the molar content of lithium oxide was found. On the other hand, some relationships were found by the Li_2O influence on the Si Q-distribution and P Q-distribution (Table 5). First the mutual relationships between Si Q-units and between P Q-units were found. Increase of Li content increases SiQ^0, SiQ^1, and SiQ^2, and simultaneously decreases the amount of SiQ^3, and SiQ^4. Similarly, Li content increases PQ^0 and decreases PQ^1 and PQ^2.

It was found that SiQ^0, SiQ^1, and SiQ^2 are strongly positively correlated (Table 6). Similarly, SiQ^3, and SiQ^4 are strongly positively correlated. The strong positive correlation means that correlated quantities are changed proportionally in the same direction. Thus, decreasing of the content of SiQ^3, and SiQ^4 (caused by decreasing of the degree of networking) leads to increase of SiQ^0, SiQ^1, and SiQ^2. Similarly, it is with phosphate Q-units. It was found that PQ^1 and PQ^2 are strongly positively correlated, and PQ^0 is strongly negatively correlated with PQ^1 and PQ^2. Thus, decreasing of the content of PQ^1, and PQ^2 (caused by decreasing of the degree of networking) leads to increase of PQ^0.

In the next step the correlation analysis between the measured properties an Si Q-distribution and P Q-distribution was analyzed (Table 7). As can be expected for the viscous flow activation energy and the glass transition temperature the strong negative correlation was found with SiQ^0, SiQ^1, SiQ^2, and PQ^0. Simultaneously the strong positive correlation was identified for SiQ^3, SiQ^4, PQ^1, and PQ^2. It confirmed that decreasing the degree of networking decreases the values of E_{η^*}, and T_g. On the other hand, the correlation analysis of the thermal expansion coefficients does not show strongly significant correlations. But in principle (i.e., according to the signs of correlation coefficients) it confirms that decreasing the degree of networking increases the thermal expansion coefficients.

Conclusions

According to the presented results of SV TDM the 45S5 Bioglass® doped Li_2O bioactive glass can be considered as a homogeneous mixture of 9, or 10 components were present in significant equilibrium molar amount for each studied glass composition. In all glass compositions containing nonzero amount of Li_2O, the four lithium compounds with not negligible equilibrium amount were identified, i.e. $Li_2O{\cdot}SiO_2$, $3Li_2O{\cdot}P_2O_5$, $Li_2O{\cdot}2CaO{\cdot}2SiO_2$, and $2Li_2O{\cdot}SiO_2$. In the 45S5 glass composition four phosphate compounds with not negligible abundance were identified: $9Na_2O{\cdot}6SiO_2{\cdot}2P_2O_5$, $Na_2O{\cdot}2CaO{\cdot}P_2O_5$, $5Na_2O{\cdot}4SiO_2{\cdot}P_2O_5$, and $Na_2O{\cdot}CaO{\cdot}P_2O_5$. In all other glasses the $3Li_2O.P_2O_5$ was found with not negligible abundance. Moreover, in the glass with 4.1 mol% Li_2O the $Na_2O{\cdot}2CaO{\cdot}P_2O_5$ and $3Li_2O{\cdot}P_2O_5$ compounds were found with not negligible abundance. The viscous flow activation energy and the glass transition temperature the strong negative correlation was found with SiQ^0, SiQ^1, SiQ^2, and PQ^0. Simultaneously the strong positive correlation was identified for SiQ^3, SiQ^4, PQ^1, and PQ^2. It confirmed that decreasing the degree of networking decreases the values of E_{η^*}, and T_g.

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