

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
20 (2014)

**THERMODYNAMIC MODEL AND VISCOSITY
OF As-Se GLASSES**

Jozef CHOVANEC, Jana SHÁNĚLOVÁ and Jiří MÁLEK¹
Department of Physical Chemistry,
The University of Pardubice, CZ–532 10 Pardubice

Received March 31, 2014

This work is focused on study of structure and viscosity relationship of As-Se glass melts. The structure was described by the thermodynamic model (or model of association solutions) of Shakhmatkin and Vedishcheva. The system contains five components (As, Se, AsSe, As₂Se₃, As₄Se₃) according to the phase diagrams. In this model, we consider only four components because the last one is in linear dependence on the As amounts. For a description of experimental viscosity values, we used the regular Adam & Gibbs, Avramov and Milchev and MYEGA viscosity equations. The thermodynamic model described the structural units in the As-Se undercooled glasses with sufficient precision. The best fit of viscosity data was achieved using the Adam & Gibbs model.

¹ To whom correspondence should be addressed.

Introduction

Chalcogenide glasses have high transmittance in the infrared region, low phonon energies, and significant nonlinearity of their optical properties. Therefore, they have been the subject of intense pure and applied research for a long time [1-3]. The arsenic selenide glasses are interesting materials which can be used as materials for optical fibers [4-6]. One of the most important physical properties examined in long term is viscosity [7]. The viscosity of As-Se system was studied by several authors [8-11].

In the present work, the experimental temperature dependence of viscosity of $\text{As}_x\text{Se}_{(1-x)}$ (from $x = 0$ to 0.54) undercooled melts was obtained from Nemilov [8]. We applied various viscosity models, Vogel–Fulcher–Tammann’s model [12-14], Adam and Gibbs [15,16], Avramov and Milchev [17], and MYEGA [18]. The compositional dependence of the parameters of applied viscosity models were described by multilinear forms using the overall atomic glass composition (mole fractions x_g (As) and x_g (Se)) as independent variables, and the equilibrium molar amounts of components were calculated in the thermodynamic model of Shakhmatkin and Vedishcheva.

Methods

Shakhmatkin and Vedishcheva Thermodynamic Model

The model [19-22] assumed that the standard Gibbs energies of binary crystalline phases and the compositions of systems are used as the input data. An advantage of this model is that it does not contain any next adjustable parameters except the standard Gibbs energies. The melts are considered as ideal equilibrium solutions which contain unreacted input entities and reactants which were created in the chemical equilibrium. The products have the same stoichiometry as the crystalline compounds in the equilibrium phase diagram. We are looking for the combination of molar amounts n_i (they must comply with material balance of both elements) when the Gibbs energy is minimal [23]. The total Gibbs energy is expressed as follows by assuming ideal solution

$$G(n_1, n_2, \dots, n_N) = \sum_{i=1}^N N_i G_{m,i} + RT \sum_{i=1}^N \frac{n_i \ln n_i}{\sum_{j=1}^N n_j} \quad (1)$$

where T is the temperature of system, N is the number of species, n_i is the molar amount of i -th species and $G_{m,i}$ is the molar Gibbs energy of pure i -th species at the

pressure and temperature of the system. For the particular glass at temperature T lower than T_g , $T = T_g$ is used. It means it is supposed that the glass structure is frozen at T_g .

The thermodynamic model was calculated by program JaneDove which was programmed in FORTRAN. This software was used in other works [24-26].

Temperature Dependence of Viscosity

The temperature dependence for particular glass composition is described with a sufficient accuracy using the three parametric viscosity equation. The viscosity equations mentioned earlier are summarized in the final form used for a regression treatment. The details of these can be found in our previous work [27].

a) Vogel–Fulcher–Tammann’s viscosity equation [12-14]

$$\log \eta = \log \eta_{\infty} + \frac{B}{T - T_0} \quad (2)$$

This equation corresponds to temperature dependent value of activation energy E_{η}^* , i.e.,

$$E_{\eta}^* = R \frac{\partial \ln \eta}{\partial (1/T)} = 2.303 R \frac{\partial \log \eta}{\partial (1/T)} = 2.303 R \frac{T^2 B}{(T - T_0)^2} \quad (3)$$

If T_g^{12} is defined by $\log [\eta(T_g)/\text{Pa s}] = 12$ then

$$T_g = \frac{B}{12 - \log \eta_{\infty}} + T_0 \quad (4)$$

Fragility, m , was obtained from the definition

$$m = \left[\frac{\partial \log \eta(T)}{\partial (T_g/T)} \right]_{T=T_g} = (12 - \log \eta_{\infty}) \frac{T_g}{T - T_0} \quad (5)$$

b) Adam and Gibbs configuration entropy equation [15]

$$\log \eta = \log \eta_{\infty} + \frac{1}{T \left[\frac{1}{T_g (12 - \log \eta_{\infty})} + \frac{\Delta c_p}{B} \ln \frac{T}{T_g} \right]} \quad (6)$$

The fragility can then be calculated from

$$m = (12 - \log \eta_{\infty}) \left[1 + \frac{\Delta c_p T_g (12 - \log \eta_{\infty})}{B} \right] \quad (7)$$

c) Avramov and Milchev equation [17]

$$\log \eta = \log \eta_{\infty} + (12 - \log \eta_{\infty}) \left(\frac{T_g}{T} \right)^{\alpha} \quad (8)$$

where

$$\alpha = \frac{m}{12 - \log \eta_{\infty}} \quad (9)$$

d) MYEGA equation [18]

$$\log \eta = \log \eta_{\infty} + (12 - \log \eta_{\infty}) \frac{T_g}{T} \exp \left[(\alpha - 1) \left(\frac{T_g}{T} - 1 \right) \right] \quad (10)$$

Accounting for Viscosity Compositional Dependence

In all viscosity equations, the high temperature limit of viscosity value, $\log \eta_{\infty}$ (marked as A), represents one of the estimated parameters. Generally, it is supposed that this parameter is independent of the composition [16]. In our work, we deal with two cases when the parameter is composition-dependent (AV) and composition-independent (AC).

For each of the viscosity model, the viscosity–composition dependence can be expressed by the unknown parameters (e.g., $\log \eta_{\infty}$, B , Δc_p , and α) as multilinear forms of molar amounts of system components.

a) In the first case (the glass model), the independent variables are used for multilinear dependence of each unknown parameter. The values of unknown parameters are expressed as multilinear forms of system composition (x_{As} , x_{Se}) by the following way

$$\log \eta_{\infty} = \sum_{i=1}^2 a_i x_i \quad (11)$$

$$B = \sum_{i=1}^2 b_i x_i \quad (12)$$

$$\Delta c_p = \sum_{i=1}^2 c_i x_i \quad (13)$$

$$\alpha = \sum_{i=1}^2 \alpha_i x_i \quad (14)$$

b) The second possibility is the use the thermodynamic model. There, the equilibrium molar amounts, n_i , are used as independent variables. These values are for 1 mol of glass constrained by

$$n(\text{As}) + n(\text{Se}) + 2n(\text{AsSe}) + 5n(\text{As}_2\text{Se}_3) + 7n(\text{As}_4\text{Se}_3) = 1 \text{ mol} \quad (15)$$

The values of unknown parameters are expressed as multilinear forms of system composition

$$\log \eta_{\infty} = \sum_{i=1}^2 a_i n_i \quad (16)$$

$$B = \sum_{i=1}^2 b_i n_i \quad (17)$$

$$\Delta c_p = \sum_{i=1}^2 c_i n_i \quad (18)$$

$$\alpha = \sum_{i=1}^2 \alpha_i n_i \quad (19)$$

In both cases, the unknown parameters are obtained by a nonlinear regression analysis with significant parameters identified at the 95 % significance level by the Student's t -value.

Results and Discussion

For the description of experimental viscosity values of As-Se undercooled glasses, we used Vogel–Fulcher–Tammann's viscosity equation. The viscosity data were obtained from the article by Nemilov [8]. The parameter of fragility, m , and viscous flow activation energy, E_{η}^{\ddagger} , at the glass transition temperature were calculated for each glass composition (Table I).

Table I Glass compositions, parameters of VFT equations, glass transition temperature T_g , standard deviation of approximation s_{appr} , viscous flow activation energy E_h^\ddagger , and fragility m

$x_{gl}(As)$	$T_g^{(12)}$ K	$\log(\eta_\infty / Pa \cdot s)$ ($s(\log \eta_\infty)$)	B / K ($s(B)$)	T_0 / K	s_{appr}	$E_{\eta^\ddagger}(T_g)$ kJ mol ⁻¹	m
0	303.15	-1.11 ± 0.67	744.0 ± 99.6	246.2 ± 4.8	0.1	406.1	70
0.01	307.65	-0.16 ± 0.57	549.2 ± 72.0	262.5 ± 3.9	0.1	488.3	83
0.03	316.15	-0.11 ± 0.38	563.4 ± 60.4	268.8 ± 3.8	0.19	495.2	82
0.05	320.15	-0.64 ± 0.22	624.9 ± 36.7	270.5 ± 2.2	0.1	501	82
0.1	331.15	-1.87 ± 0.50	939.3 ± 104.2	265.0 ± 5.4	0.19	434.5	68
0.149	344.15	-2.19 ± 0.44	1139.1 ± 108.5	265.1 ± 5.5	0.15	403.5	61
0.1825	351.15	-7.09 ± 1.25	2756.2 ± 480.9	209.3 ± 16.3	0.2	316.8	47
0.25	364.15	-7.76 ± 0.94	3678.0 ± 463.5	179.1 ± 15.0	0.13	271.1	39
0.265	365.15	-8.20 ± 1.18	4361.6 ± 666.9	151.0 ± 21.1	0.16	241.2	34
0.286	370.65	-10.82 ± 1.25	5854.1 ± 811.8	115.7 ± 22.0	0.12	236.1	33
0.293	376.15	-11.65 ± 1.38	6425.7 ± 940.0	106.6 ± 24.4	0.12	238.5	33
0.35	392.15	-9.92 ± 1.90	5824.0 ± 1288.5	129.8 ± 36.8	0.21	247.1	33
0.38	417.15	-7.46 ± 1.96	4259.2 ± 1037.0	199.6 ± 31.7	0.11	298.2	37
0.4	443.15	-5.95 ± 1.38	2899.5 ± 559.6	282.1 ± 19.1	0.12	418.8	49
0.422	437.15	-5.06 ± 0.50	2802.0 ± 231.8	274.6 ± 9.1	0.1	383	46
0.433	435.15	-7.99 ± 0.79	4482.2 ± 463.5	211.8 ± 14.8	0.1	324.3	39
0.45	433.15	-8.11 ± 0.89	4803.9 ± 550.7	194.7 ± 17.2	0.1	303	37
0.485	425.65	-6.59 ± 0.36	4039.1 ± 214.0	209.0 ± 7.5	0.1	297.7	36
0.49	431.15	-6.92 ± 0.59	3958.0 ± 332.2	223.2 ± 11.4	0.1	323.6	39
0.5	440.15	-2.73 ± 0.40	1825.8 ± 148.5	316.7 ± 7.1	0.11	442	52
0.506	426.15	-4.56 ± 0.52	2885.5 ± 256.6	252.0 ± 10.5	0.1	330.6	41
0.51	425.15	-5.59 ± 0.45	3433.1 ± 241.0	228.8 ± 9.1	0.1	310.2	38
0.527	422.15	-2.93 ± 0.26	1906.0 ± 99.7	295.5 ± 4.7	0.1	400.8	49
0.537	415.15	-1.44 ± 0.20	1361.4 ± 63.2	314.7 ± 3.4	0.1	439.7	55

In Fig. 1, it can be seen that the glass transition temperature increases with an increasing content of arsenic, and the glass transition temperature reaches a maximum value (for the experimental values) for the stoichiometric composition of As_2Se_3 with $x_{gl}(As) = 0.4$. The maximum for thermodynamic model is shifted

to a higher concentration of As ($x(\text{As}) = 0.45$). This is related to the higher dispersion of T_g at a larger amount of As (this dispersion is marked by circle) which shifted the curve of thermodynamic model.

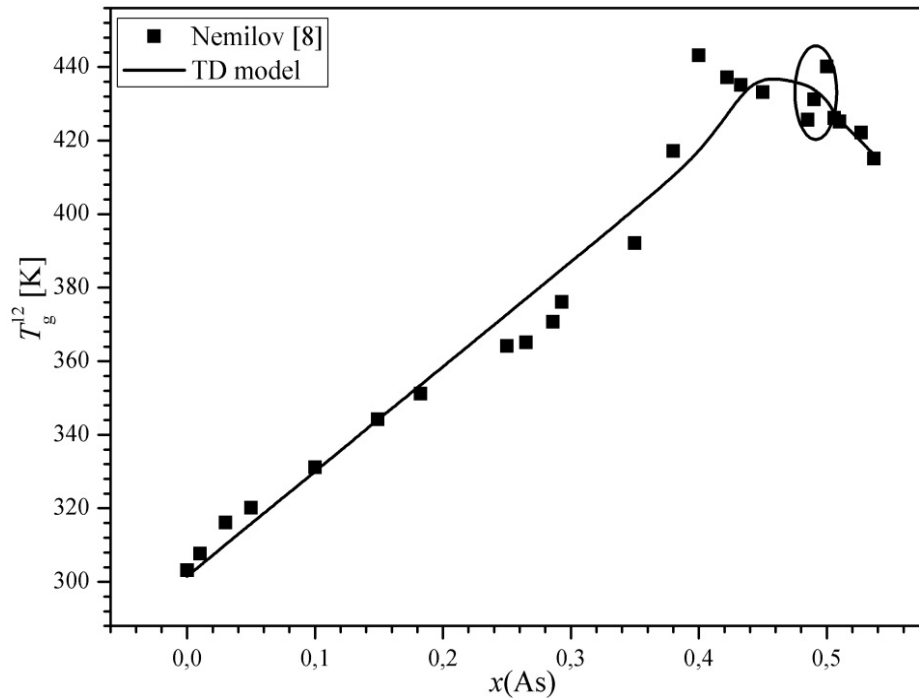


Fig. 1 Dependence of T_g^{12} upon temperature

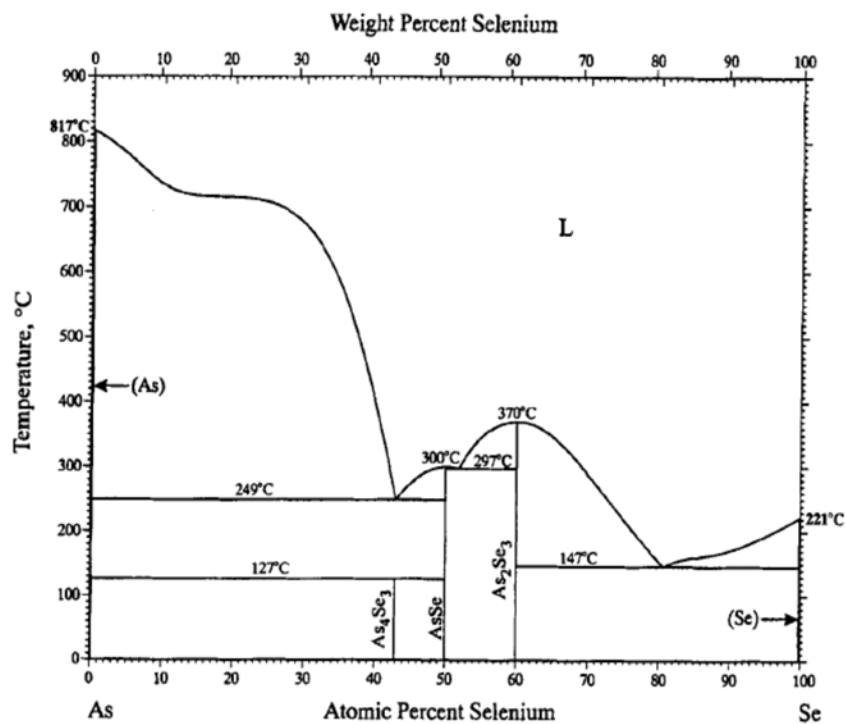


Fig. 2 Phase diagram of As-Se system

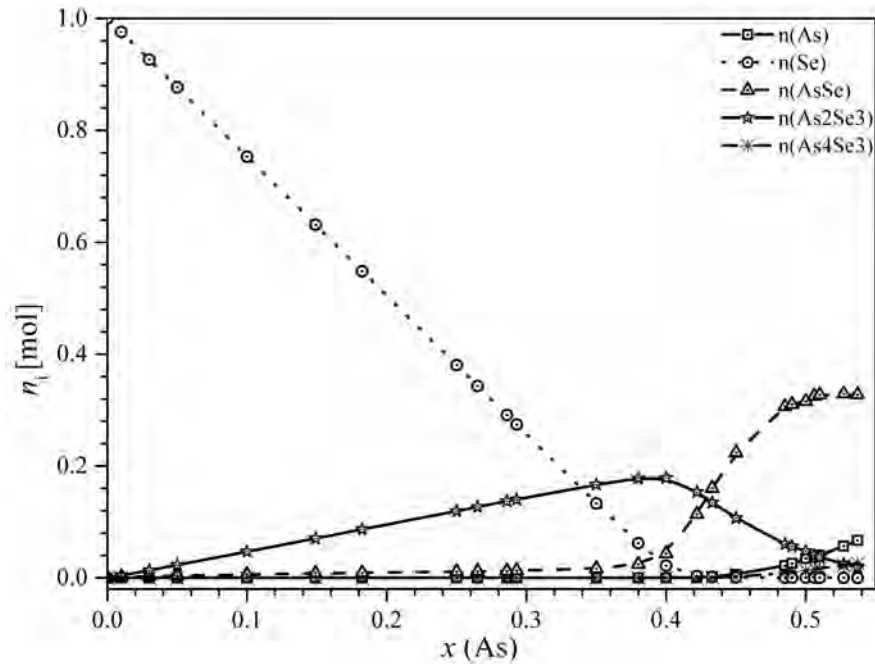


Fig. 3 Equilibrium molar amount of system components at T_g^{12}

It is evident from the phase diagram in Fig. 2 that the As-Se system contains three crystalline phases (As_4Se_3 , AsSe and As_2Se_3). In addition, this system contains entities As and Se.

The thermodynamic model was evaluated for each glass composition at T_g^{12} temperature. We assumed that under this temperature the glass is already frozen. Due to significant positive correlations between equilibrium molar amounts of As and As_4Se_3 , only four components were considered in the regression treatment (As, Se, AsSe, As_2Se_3). The substantial changes in molar amount of all components in equilibrium take place with increasing content of As (Fig. 3). It is worth noting that for $x_{\text{gl}}(\text{As}) = 0.4$ the system consists of large amount of structural units of As_2Se_3 as a majority and a part of AsSe and unreacted Se as a minority. The molecular structure of As_2Se_3 is described as a random network where Se chain fragments are crosslinked by pyramidal $\text{AsSe}_{3/2}$ units [28,29]. The structure of crystalline As_2Se_3 consists of layers. Inside the layers, the atoms are connected by strong covalent bonds and individual layers are linked together by the van der Waals bonds with minor covalent component [30]. Therefore, the structure in the system, where there is a greater amount of As_2Se_3 , is more rigid. For the lower As content, the system is composed of the mixture of unreacted Se (the amount decreases) and As_2Se_3 (rises with increasing amount of As). For the higher amount of As (over 0.4), the content of As_2Se_3 decreases and it is combined with AsSe and a small amount of unreacted of As. This explains the non-monotonous compositional dependence of T_g (i.e., T_g^{12}) that reaches the maximum value at $x_{\text{gl}}(\text{As}) = 0.4$. It is obvious that the rise of the value of T_g is related to the amount of produced structure units of As_2Se_3 . The influences of other components are

lower.

The T_g compositional dependence was described (with the standard deviation of approximation of 9.1 K) on the basis of the thermodynamic model by following equation

$$T_g^{12} = (1042.0 \pm 209.2)n(\text{As}) + (301.5 \pm 4.3)n(\text{Se}) + (937.3 \pm 28.5)n(\text{AsSe}) + (2073.1 \pm 23.9) \quad (19)$$

If the amount of arsenic rises, the viscosities are shifted towards higher temperature (Fig. 4.). According to the thermodynamic model, the cyclic and ring structures of Se are broken and the As_2Se_3 structural units are created. The structure of glasses becomes more rigid and the maximum of rigidity is reached if the amount of As is equal to 0.4. The next addition of As causes the shift of viscosity curves to lower temperatures as the amount of As_2Se_3 units decreases and the system produces AsSe units. The AsSe becomes majority unit at the content of $x(\text{As}) = 0.5$ as we can see in Fig. 3. The shift of viscosity curves to lower temperatures at the higher amount of As is less significant, because more structural units (e.g., if $x(\text{As}) = 0.5$, the undercooled melts contain AsSe, As_2Se_3 , As and a small amount of As_4Se_3)

Table II Results of nonlinear regression analysis of experimental viscosity data; s_{appr} – standard deviation of approximation of $\log(\eta/\text{Pa s})$, F – Fisher's statistics. The $\log(\eta_{\infty}/\text{Pa s})$ is reported only for the AC models

Model	s_{appr}	F	$\log(\eta_{\infty}/\text{Pa s})$
MY-GL-AC	0.49	30	-1.41 ± 0.39
MY-TD-AC	0.4	45	-1.44 ± 0.32
MY-GL-AV	0.49	30	-
MY-TD-AV	0.37	52	-
AM-GL-AC	0.49	30	NSS ⁺
AM-TD-AC	0.4	45	NSS
AM-GL-AV	0.49	30	-
AM-TD-AV	0.38	51	-
AG-GL-AC	0.38	51	-3.13 ± 0.27
AG-TD-AC	0.68	16	-2.14 ± 0.41
AG-GL-AV	0.36	55	-
AG-TD-AV	0.35	58	-

⁺NSS – not statistically significant on 95% significance level

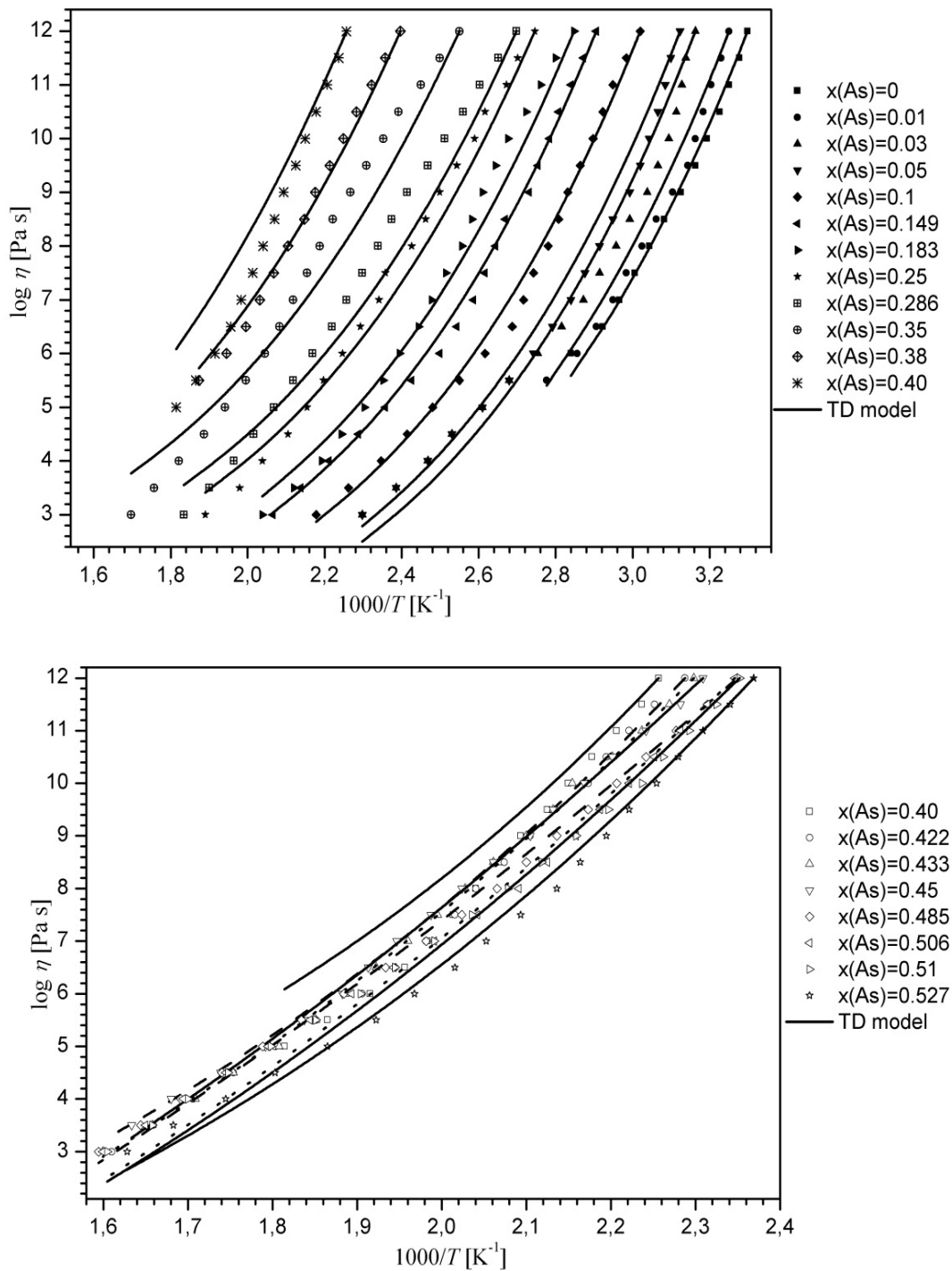


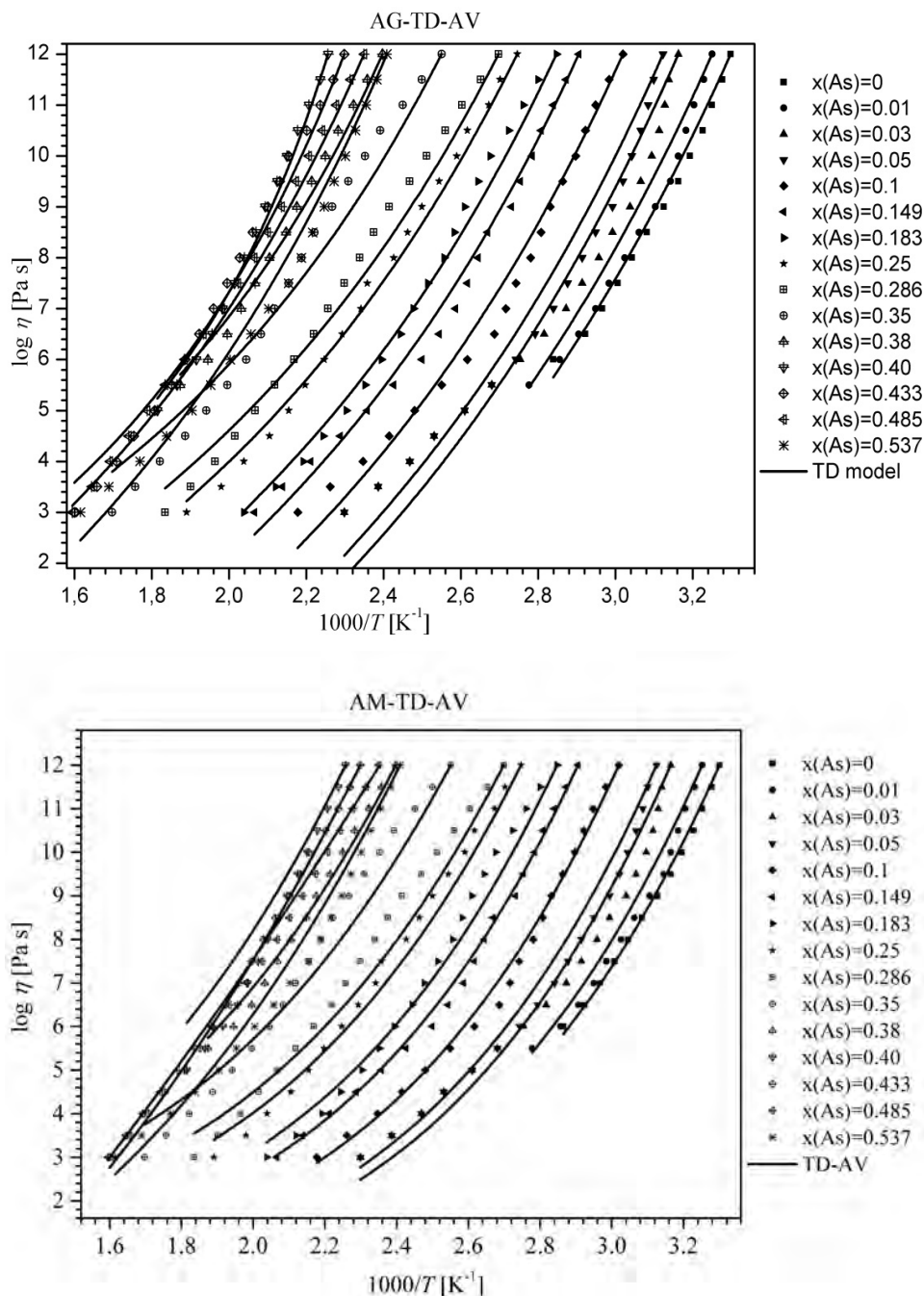
Fig. 4 Experimental and theoretical calculated viscosity values for As-Se system

are created in the system. Besides the viscosity data, Fig. 4 also contains the resultant viscosity curves from thermodynamic model of viscosity equations which will be discussed below.

For the nonlinear regression analysis, we used the software Statistica[®] vers. 12 [31]. The sum of squares between the experimental and calculated $\log(\eta/\text{Pa s})$ values was minimized. The basic statistical characteristics are summarized in Table II together with the values of statistically significant estimates of

composition independent $\log(\eta_{\infty}/\text{Pa s})$ values for “AC” models.

In Table II, we can see the standard deviations of approximation s_{apr} values for each glass. It is obvious that mainly thermodynamics models reproduce the experimental data with the accuracy approaching close the experimental error. According to the F -statistic, the best results are obtained for Adam & Gibbs thermodynamic model with $\log \eta_{\infty}$ as dependent on composition (AG – TD – AV). This model offers the lowest value of s_{apr} . Very good results were reached for the thermodynamic models calculated according to the model of Avramov & Milchev (AM-TD-AV) and MYEGA (MY-TD-AV).



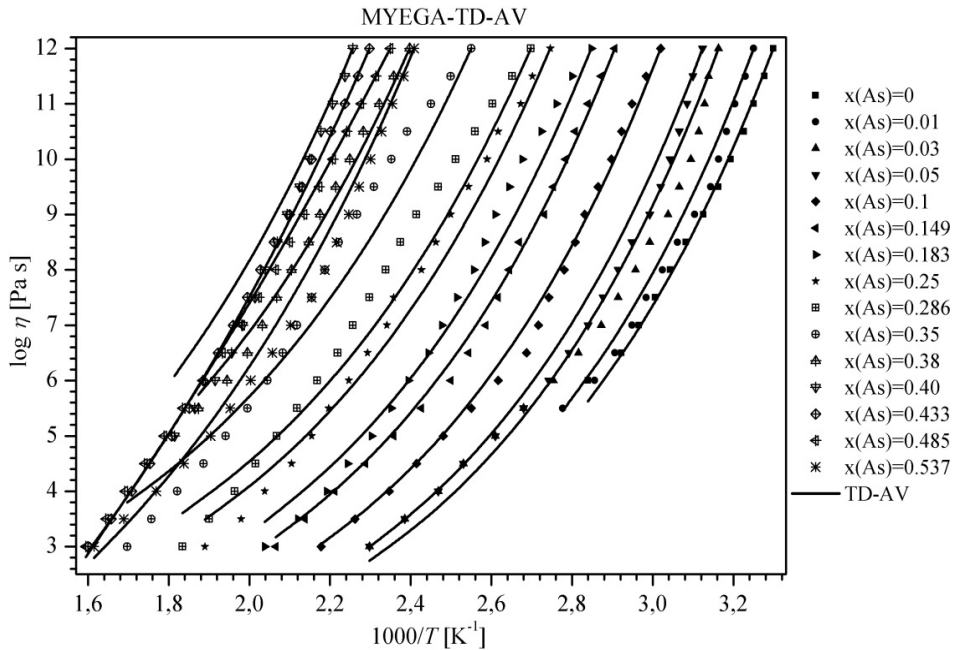


Fig. 5 Comparison of experimental and calculated $\log \eta$ values for TD-AV models

For these best models, the experimental and calculated viscosity dependences on temperature are shown in Fig. 5. It can be seen that in each case the thermodynamic model approximates the experimental data satisfactorily. The need of using the thermodynamic model is supported by the fact that it is principally impossible to describe the non-monotone T_g compositional dependence (Fig. 1) by multilinear form expressed by total selenide glass composition (i.e., by the GL-model, which is known as additive model).

The thermodynamic model includes structure units which were created in the system during melting. Therefore, it better describes the viscosity behaviour as an additive model (marked in this present work as glass model) as we can see in Fig. 6 for selected curves of viscosity dependence on temperature for Adam & Gibbs and Avramov & Milchev, or in Table II.

The change in the viscosity when the temperature approaches the glass transition temperature T_g can be used for classification of “strong” and “fragile” and the glass-forming liquids as “kinetic fragility m ” (see Eqs (5) and (13)) [32]. The “strong” systems are characterized by a spatial network with covalent bonds. A typical representative of the “strong” melts is SiO_2 with $m = 20$. On the other hand, the “fragile” systems, for example *o*-terphenyl ($m = 80$), are composed of molecular units connected by isotropic bonds of Van der Waals type [33].

The fragility gives us the possibility to compare the slopes of experimental and calculated viscosity temperature dependence or, more precisely, the slope of the $\log \eta$ versus T_g/T dependence. The comparison of fragility as a function of amount of As for values calculated from thermodynamic model is presented in Fig. 7.

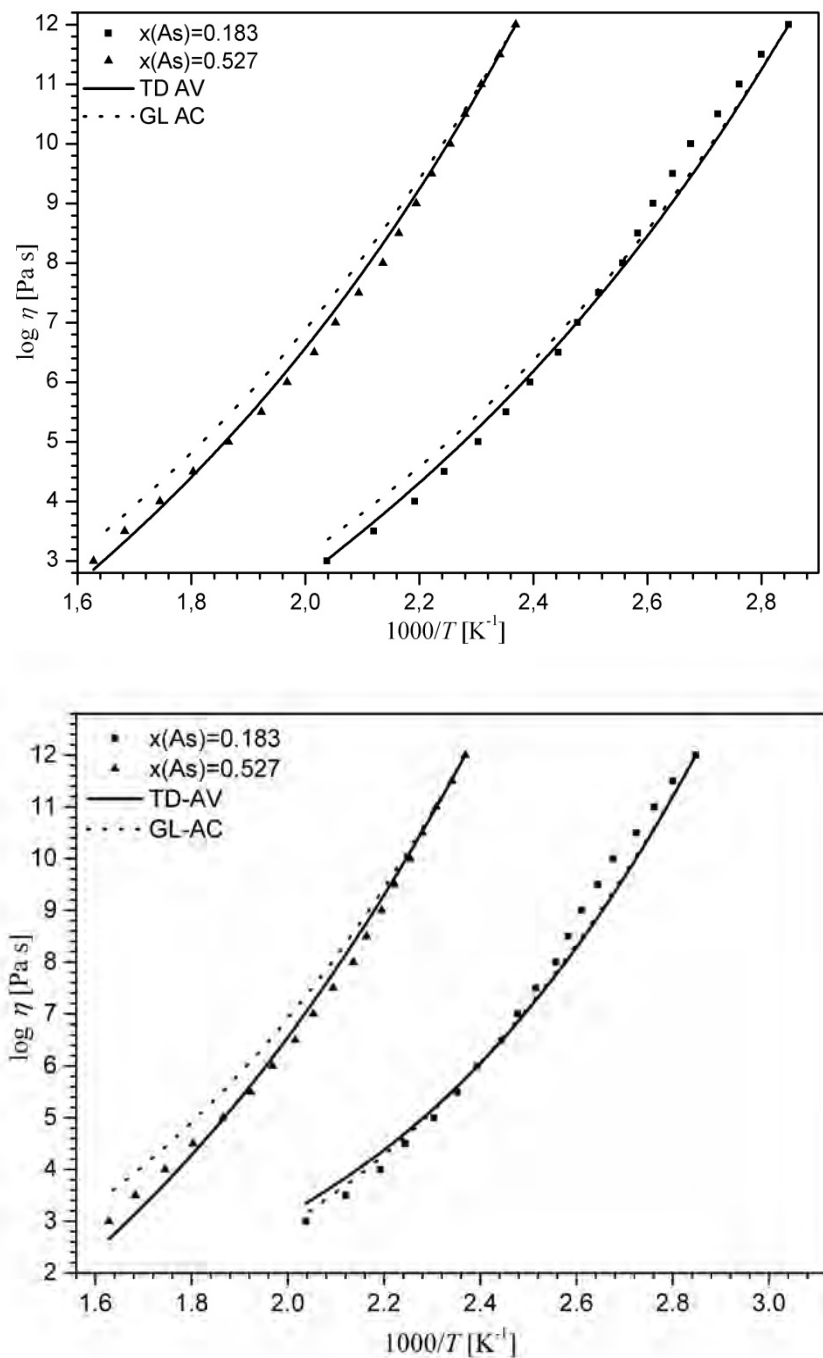


Fig. 6 Comparison of experimental and calculated $\log \eta$ values for TD-AV and GL-AC models for selected curves of Adam & Gibbs and Avramov & Milchev

If the concentration of As is minimum, the glass contains mainly unreacted Se, which creates only rings and cycles as molecular units. Thus, the undercooled melt is more “fragile”. The structure units of As_2Se_3 are created in the system with increasing amount of As. The undercooled melt becomes “strong”. For the composition of $x(\text{As}) = 0.40$, the fragility achieves the value $m = 38.6$ for Avramov & Milchev, 39.6 according to MYEGA, and $m = 55.6$ for Adam & Gibbs. These values for AM and MYEGA are almost identical with the value

which was obtained by Málek *et. al.* [34]. According to them, the experimental value of fragility of As_2Se_3 glasses was $m = 38$.

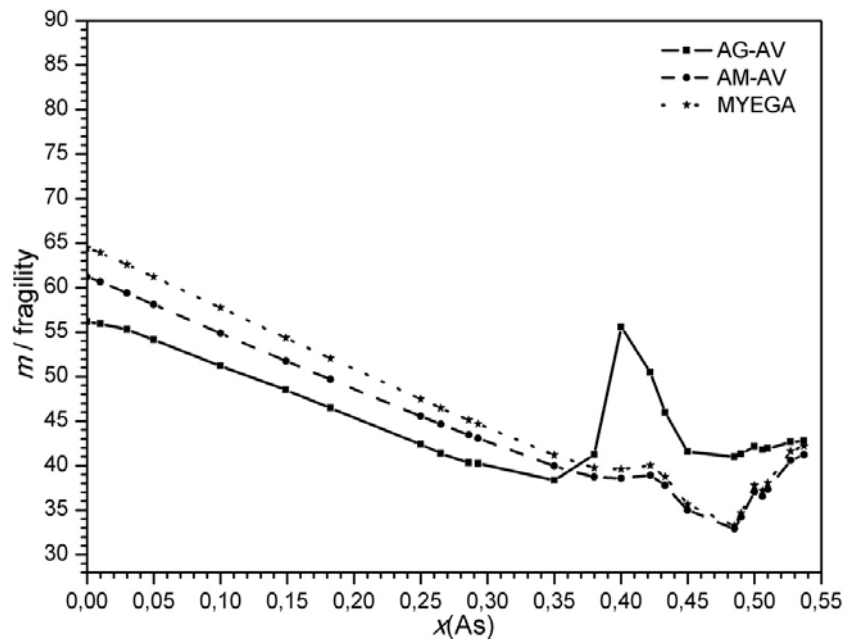


Fig 7 Comparison of calculated fragility values for different models

Table III Results of nonlinear regression analysis for thermodynamics AV models, NSS — not statistically significant; b/α — means b for AG and α for AM and MY

	AG-AV	AM-AV	MY-AV
a (As)	-19.34 ± 4.95	159.0 ± 17.6	367.55 ± 16.63
a (Se)	-6.99 ± 0.28	NSS	NSS
a (AsSe)	-8.05 ± 1.35	-35.06 ± 3.46	-42.34 ± 4.04
a (As_2Se_3)	NSS	12.99 ± 1.49	9.68 ± 1.68
b/α (As)	100	51.27 ± 4.34	42.71 ± 3.67
b/α (Se)	-4.85 ± 1.39	5.10 ± 0.07	4.59 ± 0.06
b/α (AsSe)	-0.95 ± 0.15	-1.60 ± 0.50	-1.97 ± 0.45
b/α (As_2Se_3)	0.48 ± 0.11	19.09 ± 0.93	17.22 ± 0.83
c (As)	0.02 ± 0.00	-	-
c (Se)	0.00 ± 0.00	-	-
c (AsSe)	NSS	-	-
c (As_2Se_3)	NSS	-	-

The calculated parameters for choosing the best models (thermodynamic, with composition dependent) are summarized in Table III. From Table II we can see that the physical meanings of these models are much closed, according to Avramov & Milchev and MYEGA (the s_{appr} and Fisher's statistics are equal). Moreover, in some cases relatively high standard deviations and their differences are observed. Some differences in s_{appr}/F are between AM/MYEGA and AG. The Adam & Gibbs viscosity equation contains more degrees of freedom. The different number of statistically significant members was retained in different multilinear forms. It should be considered that the b and c coefficients are not defined unambiguously (see Adams & Gibbs — Eq. (6) — one of the parameters of b was kept constant). Thus the physical meaning of the obtained numerical values of parameters (mainly Δc_p in the Adam and Gibbs equation) can be questionable.

Conclusion

The experimental viscosity data of undercooled melts of As-Se system were described by viscosity equations — Adam and Gibbs, Avramov and Milchev, and MYEGA. The parameters of these models were obtained on the basis of the thermodynamic model and additive model. The thermodynamic model of Shakhmatkin and Vedishcheva considers the structural units as As, Se, AsSe, and As₂Se₃, which were created in the thermodynamics equilibrium at glass transition temperature, while in the case of additive model, only the arsenic and selenium were considered. The statistically more robust description was obtained using the thermodynamics model. In both models, we used the high temperature viscosity limits as independent and dependent on compositions. The experimental data are better described using composition dependent variant of $\log \eta_\infty$ parameter. From the statistic point of view, the thermodynamic model according to Adam & Gibbs was the best, but the fragility is not described very well. Thus, the models of Avramov & Milchev and MYEGA are suitable to describe of viscosity dependences in As-Se system, too.

Acknowledgement

This work was supported by the Operational Program Research and Development funded from the European Fund of Regional Development. The Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 "Strengthening of Research and Development Teams at the University of Pardubice", financially supported this work.

References

- [1] Li W., Seal S., Rivero C., Lopez C., Richardson K., Pope A., Schulte A., Myneni S., Jain H., Antoine K., Miller A.C.: *J. Appl. Phys.* **98**, 053503 (2005).
- [2] Carlie N., Musgraves J.D., Zdyrko B., Luzinov I., Hu J., Singh V., Agarwal A., Kimerling L.C., Canciamilla A., Morichetti F., Melloni A., Richardson K.: *Opt. Expr.* **18**, 26728 (2010).
- [3] Varshneya A.K., (Sheffield 2006).
- [4] Duhant M., Renard W., Canat G., Troles J., Toupin P., Brilland L., Smektala F., Betourne A., Bourdon P., Renversez G.: *Fib. Las. Techn., Syst., Appl.* **9**, 8237 (2012).
- [5] Lukacs R., Kugler S.: *Jpn. J. Appl. Phys.* **50**, 091401 (2011).
- [6] Nguyen T.N., Chartier T., Coulombier Q., Houizot P., Brilland L., Smektala F., Troles J., Thual M., 14th OptoElectronics and Communications Conference, 534 (2009).
- [7] Rao K.J.: *Structural Chemistry of Glasses*, Elsevier Science Ltd, Oxford, 1 (2002).
- [8] Nemilov S. V: *J. Appl. Chem.-USSR* **36**, 977 (1963).
- [9] Kunugi O.R.M., Suzuki M.: *J. Soc. Mater. Sci. Jpn.* **19**, 145 (1970).
- [10] Bernatz K.M., Echeverria I., Simon S.L., Plazek D.J.: *J. Non-Cryst. Solids* **307**, 790 (2002).
- [11] Musgraves J.D., Wachtel P., Novak S., Wilkinson J., Richardson K.: *J Appl. Phys.* **110**, 063503 (2011).
- [12] Vogel H.: *Physikalische Zeitschrift* **22**, 2 (1921).
- [13] Fulcher G.S.: *J. Am. Ceram. Soc.* **8**, 389 (1925).
- [14] Tammann G., Hesse W.: *Zeit. anorg. allgem. Chem.* **156**, 245 (1926).
- [15] Adam G., Gibbs J.H.: *J.Chem. Phys.* **43**, 139 (1965).
- [16] Ojovan M.I.: *Phys. Chem. Glass. - Eur. J. Glass Sci. Tech., Part B* **53**, 143 (2012).
- [17] Avramov I., Milchev A.: *J. Non-Cryst. Solids* **104**, 253 (1988).
- [18] Mauro J.C., Yue Y., Ellison A.J., Gupta P.K., Allan D.C.: *Proc. Nat. Ac.Sc.* **106**, 19780 (2009).
- [19] Shakhmatkin B.A., Vedishcheva N.M., Shultz M.M., Wright A.C.: *J. Non-Cryst. Solids* **177**, 249 (1994).
- [20] Vedishcheva N.M., Shakhmatkin B.A., Shultz M.M., Wright A.C.: *J. Non-Cryst. Solids* **196**, 239 (1996).
- [21] Vedishcheva N.M., Shakhmatkin B.A., Wright A.C.: *J. Non-Cryst. Solids* **293**, 312 (2001).
- [22] Wright A.C., Shaw J.L., Sinclair R.N., Vedishcheva N.M., Shakhmatkin B.A., Scales C.R.: *J. Non-Cryst. Solids* **345**, (2004).
- [23] Vonka P., Leitner J.: *Coll. Czech. Chem. Comm.* **65**, 1443 (2000).

- [24] Chromčíková M., Liška M., Gasparková E., Teplanová M., Karell R.: *Ceram.-Silik.* **57**, 66 (2013).
- [25] Chromčíková M., Liška M., Karell R., Gasparková E., Vlková P.: *J. Therm. Anal. Cal.* **109**, 831 (2012).
- [26] Chromčíková M., Liška M., Macháček J., Šulcová J.: *J. Therm. Anal. Cal.* **114**, 785 (2013).
- [27] Chovanec J., Chromčíková M., Liška M., Shánělová J., Málek J.: *J. Therm. Anal. Cal.* **116**, 581 (2013).
- [28] Sagara Y., Uemura O., Okuyama S., Satow T.: *Phys. Stat. Solid. A-Appl. Res.* **31**, K33 (1975).
- [29] Crozier E.D., Lytle F.W., Sayers D.E., Stern E.A.: *Can. J. Chem.-Rev. Can. Chim.* **55**, 1968 (1977).
- [30] Stergiou A.C., Rentzeperis P.J.: *Z. Kristall.* **173**, 185 (1985).
- [31] I.S.d.a.s.s. StatSoft, Version 12. www.statsoft.com, 2013.
- [32] Angell C.A.: *J. Non-Cryst. Solids* **131**, 13 (1991).
- [33] Málek J.: *Thermochim. Acta* **311**, 183 (1998).
- [34] Málek J., Shánělová J.: *J. Non-Cryst. Solids* **351**, 3458 (2005).