Petr Koštál, Tomáš Hofírek, Jiří Málek. (2018). Viscosity measurement by thermomechanical analyzer. *Journal of Non-Crystalline Solids,vol. 480, pp. 118-122.* doi: 10.1016/j.jnoncrysol.2017.05.027

Viscosity measurement by thermomechanical analyzer

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Abstract

Original viscosity data for $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} chalcogenide glass-formers were measured by thermomechanical analyzer in the region from 10^5 to 10^{13} Pa.s. The combination of two experimental methods, penetration one and parallel-plate one, was used. Experimental details, important remarks and our experience with these methods are discussed and summarized. Experimental data for studied chalcogenides are correlated with previously measured data in Ge-Se system and also combined with previously published data for melt region. The Vogel-Fulcher-Tammann equations are used for fitting experimental and literature data and their parameters are discussed.

Keywords: viscosity; chalcogenides; thermomechanical analysis; penetration method; parallel-plate method;

Publisher
ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS
DOI: 10.1016/j.jnoncrysol.2017.05.027

1. Introduction

Viscosity is a very important physical property which determines the flow of a material. Its knowledge, description and experimental determination are important especially in the case of glass-forming materials. Preparation of glass products in defined shapes needs the knowledge of temperature dependence of viscosity of melt and undercooled melt. The viscosity also influences the processes of structural relaxation and cold crystallization which can be observed in glass and undercooled melt, respectively. The structural relaxation is a very slow rearrangement of thermodynamically unstable glass toward equilibrium. This process is in fact a very slow flow of

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material and hence it is influenced by viscosity. The connection between viscosity and structural relaxation is apparent from the similarity of apparent activation energies of both processes [1]. Moreover, structural relaxation time is proportional to viscosity through well-known Maxwell equation and the shear modulus at infinite frequency. Cold crystallization, which takes place in undercooled melt, and its connection with viscosity is also very important. The growing crystals are surrounded by undercooled melt and their growth is influenced by viscosity and diffusivity in their vicinity. Viscosity is then necessary for calculations of reduced crystal growth rate [2] which can be used for determination and theoretical description of growth mechanism [3]. The relation between viscosity and crystal growth rate was investigated recently in several works [4-7].

The temperature dependence of viscosity can be studied by thermomechanical analyzer (TMA) in vertical experimental setup. This widely used instrument allows measuring of viscosity by penetration and parallel-plate methods. However, particular care should be taken on conditions of measuring procedure to obtain the accurate data with good reproducibility. We summarized our experience with TMA viscosity measurements in this work. The accuracy of measurement is estimated by measuring of NIST glass standard and important aspects of measurement are mentioned. Chalcogenide materials $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} were used as the example of measurement. According to our best knowledge, the viscous behavior of these glass-forming materials in the region of undercooled melt and glass has not been published yet. Nevertheless, the viscosities of other compositions from Ge-Se system were studied by several authors. The dynamic viscosities in the region of undercooled melt and glass were determined by penetration method in the works of Nemilov [8] (1 – 25 at. % of germanium), Gueguen et al. [9] (10 – 30 at. % of germanium) and Pustková et al. [10, 11] (8 and 10 at. % of germanium). Senapati and Varshneya [12] (5 – 40 at. % of Ge) and Maghrabi [13, 14] (20 at. % of Ge) published dynamic viscosities measured by parallel-plate method. Perron et al. [15] also studied dynamic viscosities of melts from Ge-Se system (0.5 – 10 at. % of Ge) by rotation method. We can also find several works [16-20] dealing with kinematic viscosities of Ge-Se melts measured by torsion oscillating cup method [21, 22].

2. Experimental

The selenium samples doped by low amount of germanium (0.5 and 2 at. %) were prepared by a conventional melt-quenching method. The pure elements (5N purity) were weight into fused silica ampoule. This ampoule was subsequently evacuated (approximately to 10^{-3} Pa) and sealed. The rocking furnace was used for melting and homogenization of sample at 800°C for 20 hours. The temperature was then lowered to 500 °C for four hours. The ampoule was air-quenched afterwards. The amorphous character of the prepared glass was confirmed by X-ray diffraction. The standard commercial NIST glass NBS 711 [23] was used for determination of experimental error of viscosity measurements. Thin plates (approximately 6 x 6 mm and 2.5 mm thick) or cylinders (6 mm in the diameter and 2.5 mm thick) with parallel planes were cut from the glassy bulk and brushed by fine corundum powder from both sides.

The thermomechanical analyzer TMA CX03 (RMI, Czech Republic) was used for viscosity measurements. The instrument is able to measure change of sample height by differential capacitance displacement probe detector with linearity better than 0.1% (full scale), high sensitivity (0.01 mm resolution) and low noise (typically 0.02 mm without signal filtering). The thermal and time stability is also very good (better than 0.002 mm/K and 0.008 mm/h, respectively). This instrument is able to operate in temperature range from -50°C (cooled by use of liquid nitrogen vapors) to 800 °C. Applied force can vary up to 1 N with 1 mN step.

Thermomechanical analyzer can be used for studying of viscous behavior by two methods, the penetration method and the parallel-plate method.

Penetration method is based on measuring of penetration rate of indenter which is pushed into sample by constant force. This method was firstly described by Cox [24]. It is possible to use several shapes of indenters [25]. We use hemispherical and cylindrical indenters which are generally most frequently used. The penetration depth can be calculated from the change of height of the experimental set which consists of corundum plate, sample and corundum hemispherical indenter or stainless steel cylindrical indenter (see Fig. 1a, b). The measurement itself includes three steps. The first one is heating at 10 K/min to the required temperature using loading force of 1 mN. The next step is isothermal period (5 min) to reach the thermal equilibrium of sample. In the third step, the measurement step, the force is applied at the previously selected temperature. This step showed typical initial transient period during that the penetration rate of indenter is equilibrated. After this initial period of the last step the equilibrium value of viscosity wa s obtained. In the case of high viscosities (long measurements) the equilibrium viscosity was taken as the value that no longer changed more than 0.1% in logarithmic value within a period of 5 hours.

Different equations are used for calculation of viscosity for hemispherical and cylindrical indenters. Following equation was deduced for hemispherical indenter [26, 27]:

$$\eta = \frac{9}{32\sqrt{2r}} \frac{Ft}{h^{3/2}} \tag{1}$$

here F stands for the applied force (0.01-0.5 N), t stands for the time of penetration (300-9000 min), h stands for the penetration depth (20-200 μm) and r stands for the radius of the hemisphere (1.99 mm).

Calculation of viscosity in the case of cylindrical indenter is possible by use of following equation which was deduced by Yang [25]:

$$\eta = \frac{F}{8r(dh/dt)} \tag{2}$$

here F stands for the applied force (0.01-0.3 N), t stands for the time of penetration (30-1800 min), h stands for the penetration depth (50-200 μm) and r stands for the radius of the cylinder (0.5 mm).

The penetration method in combination with thermomechanical analyzer is typically used in viscosity interval from 10^7 to 10^{13} Pa.s. Nevertheless, according to our experience it is better to use different indenters to cover this relatively broad viscosity interval. We use cylindrical indenter for viscosity values from 10^7 to 10^{11} Pa.s and hemispherical indenter for viscosity values from 10^9 to 10^{13} Pa.s. These values of viscosity can be measured according to conditions mentioned above in the brackets behind each quantity. It should be also mentioned that both equations (Eq. 1 and 2) were deduced for penetration to infinite size sample. The size of samples mentioned in experimental part of this work is close to the lower limit for obtaining correct viscosity value. Hence it is also necessary to consider fact that the larger sample should be used for bigger indenters or larger penetration depth.

Parallel-plate method is the second method which is able to measure viscosity by thermomechanical analyzer. This method is based on measuring of height of cylindrical sample which is squeezed between two corundum parallel plates by constant force (Fig. 1c). The measurement in our case also contains three steps, same like in the case of penetration method. The following equation, which is typically written in this differential form, can be used for calculation of viscosity for a cylindrical specimen [28]:

$$\eta = \frac{2\pi F d^5}{3V(dd/dt)(2\pi d^3 + V)} \tag{3}$$

here F stands for the applied force (0.01-0.1 N), d stands for the height of specimen (~2.5 mm), V stands for the specimen volume (~70 mm^3), and t stands for time (30-240 min). The volume of sample at measuring temperature can be calculated from sample volume at room temperature and coefficients of thermal expansion of glass and undercooled melt. The required accuracy of thermal expansion coefficient data depends on a temperature range where the viscosity is determined. Only good estimation from basis thermomechanical measurement is enough for most chalcogenide materials. The higher accuracy is required for materials with higher glass transition temperature. The values of thermal expansion coefficient which were used in this work for standard NBS 711 material were published by Chromčíková and Dej [29]. The parallel-plate method is suitable for measuring the viscosities lower than the penetration method. We used it typically in the region from 10^5 to $10^{7.5}$ Pa.s (appropriate values of quantities are again mentioned in the brackets above).

Very important factor in the case of accurate measurements by thermomechanical analyzer is calibration. Two height and one weight standards are used to calibrate the TMA CX03 instrument. The temperature is calibrated by use of six pure metals (Ga, In, Sn, Pb, Zn and Al). The melting temperatures of each metal registered through the abrupt decrease of sample height were measured with constant applied force (10 mN) and under different heating rates (0.2; 0.5; 1; 2; 5 and 10 K/min). The obtained melting temperatures were plotted in the dependence of heating rate and extrapolated to 0 K/min. These extrapolated melting temperatures for all tested metals were plotted versus tabulated melting temperatures. During calibration process the special emphasis was focused on the similar sample height and its position in the TMA furnace. The furnace was cooled by liquid nitrogen vapors before measurements with pure gallium metal.

3. Results

NBS standard glass

The accuracy of our viscosity measurement realized by thermomechanical analyzer was tested by measurement of NBS 711 standard glass. This oxide glass has well described temperature dependence of viscosity. The experimental data are summarized in Fig. 2.

The well-known and widely used Vogel-Fulcher-Tammann (VFT) equation [30-32] was used for fitting these data.

$$\log\eta = A + \frac{B}{(T - T_0)} \tag{4}$$

In this equation A (also known as $\log\eta_0$ or $\log\eta_\infty$), B, and T_0 are temperature independent constants for given system. The VFT equation is in fact empirical equation but it is still the most frequently used one. There are, of course, several other models which can be used for description of temperature dependence of viscosity. Some of them also try to use parameters with physical meaning. The overview of these models can be found e.g. in the works of Ojovan [33] or Mauro et al. [34]. Both of these works introduce and discuss also a viscosity theory. The main reason for using VFT equation for describing viscosity dependence of NBS glass in Fig. 2 is that this equation is used also in the NBS glass certificate. Hence the same equation is needed for correct comparison of our experimental data with the tabulated NBS data. It is also apparent from Fig. 2 that all three above mentioned experimental setups of viscosity measurements were used. The typical conditions used for given experimental setup are mentioned in experimental section. The intervals of applied forces, times of measurements and penetration depths are mentioned under each equation used for calculation of viscosity for given experimental setup. It is probably not surprising that the higher viscosity value is measured the higher applied force and longer time of measurement is required.

Ge-Se chalcogenides

The measured viscosities of $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} undercooled melts and glasses determined by penetration and parallel-plate methods are summarized in Table 1. The experimental techniques are marked. The values of viscosity are limited from the upper side by the extreme long time which is needed to obtain real equilibrate viscosity value. This time is usually much longer than standard relaxation time of glass at given temperature and is connected with stabilization of penetration rate of indenter into sample through its surface. The lower limit is connected with cold crystallization of sample. The growing crystals strongly influence the flow of material and hence it is not possible to obtain lower viscosity data by parallel-plate method.

4. Discussion

Precision and accuracy of measurement

The precision and accuracy of penetration and parallel-plate method realized by thermomechanical analyzer was tested by use of NBS 711 standard glass. The experimental data are plotted in Fig. 2. It is apparent that the points are relatively scattered and hence the experimental data are apparently not very precise. The reason for these relatively high errors of individual data point is probably very high temperature range where the viscosities of NBS material were measured. The temperature interval was from 450 to 660 °C which is in fact upper limit of TMA usage. The instrument can be used up to 800 °C but the aluminum, the temperature standard with the highest melting temperature at our case, melts around 660 °C. Hence the NBS material was measured in interval close to the upper limit. This temperature interval is different than it is typical for chalcogenide materials. Even for GeS_2, chalcogenide material with probably highest temperature of glass transition, the measurable temperature interval is approximately from 455 °C to 510 °C [35]. Viscosity of typical chalcogenide material As_2Se_3 is measurable approximately in temperature interval from 170 to 270 °C [36] and data collected for selenium doped by small amount of germanium (Table I) are from 30 to 100 °C. The temperature interval, where the viscosity is measured, influences the precision of measurement. It is probably due to the stability of instrument signal, the possible stronger problem with the sample-indenter interface and mainly the temperature homogeneity of furnace. The last point is often neglected and is not mentioned but vertical furnaces, like in the case of thermomechanical analyzer, embody this feature. The real temperature of sample is strongly dependent on its vertical position in the furnace. This is also reason why it is extremely important to make temperature calibration of instrument very precisely. It is necessary to keep the pure metals during calibration in similar position like the measured sample. We used for example a special quartz extension in the case of parallel-plate method because the experimental setup of method is lower than in the case of penetration method (indenter is replaced by plate only) and the sample position would be different without this extension. The same extension is used also during calibration of instrument. Another reason, for higher data scattering (Fig. 2) is plotting of all the measured data even when several clear outliers can be identified. These outliers should be removed. The reason for identification the data point as outlier is usually non-typical equilibration of viscosity value. This random error is probably connected with complicate conditions on sample-indenter or sample-plate interface. The identification of outlier is not easy and some experimental experience is needed. The viscosity value can be also remeasured again on new sample. This process was not made with experimental data on Fig. 2. The important is that the accuracy of measurement, which is more important than precision of measurement, is still good even in this case where no outliers were removed. It is apparent also from Fig. 2 where the VFT fit through experimental data is plotted. It should be mentioned that the VFT fit is not plotted through experimental data only. The standard NBS data from 10^5 to $10^{0.9}$ Pa.s are also included. The reason is keeping the comparability of our VFT fit with NBS data. It is important to realize that the standard data for NBS 711 are not the real experimental data [23]. The viscosity data from several laboratories were collected and VFT fit through all data were made in broad viscosity interval from $10^{0.9}$ to 10^{11} Pa.s. The data points assigned to NBS certificate in Fig. 2 represented this VFT fit. Hence it is not possible to compare VFT fit through our data only with VFT fit published in NBS certificate because for the shape of fitting curve the interval of fitting is very important. Due to this the data from NBS certificate out of our measured range were added to our experimental data and obtained data set was fitted all together. This is, in our opinion, the best way how to compare our data with standard NBS data. The final VFT curve determined from our data is very close to data from NBS certificate. The maximum difference is not higher than 0.05 in logarithmic scale. This means that even in the case of data with relatively low precision and no outliers removing, the final accuracy of measurement is good. Nevertheless, very precise calibration and sufficient number of data points are needed.

Ge-Se glass-formers

The experimental data mentioned in Table I for $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} undercooled melts and glasses are plotted in Fig. 3 together with viscosities of Ge_1Se_{99} and Ge_3Se_{97} published by Nemilov [8]. Viscosities for pure selenium published in our previous work [37] are also depicted. The VFT equations are used for fitting experimental data.

It should be mentioned, related to previous chapter, that each measured point was plotted for $Ge_{0.5}Se_{99.5}$. And only 4 viscosity points identified as outlier were not plotted and were remeasured in the case of Ge_2Se_{98}. The precision of measurement is hence much better than for

NBS 711 standard. Reason for this behavior was mentioned in the previous chapter, it is totally different temperature range of measurement. On the other hand, there is no reason to expect that accuracy of measurement is worse in the case of different temperature interval. Hence the accuracy can be expected also around 0.05 in logarithmic scale.

It is apparent from the Fig. 3 that even small addition of germanium shift the viscosity curve to high temperature region. Not surprisingly, addition of 1, 2 or 3 at. % of germanium makes this shift more significant. This shift of viscosity curves to higher temperature region is expected and it is connected with the crosslinking of material structure. Adding of typically four-fold coordinated germanium causes the matrix to become more crosslinked. The shift can be scaled by the difference between T_{12} temperatures. T_{12} temperature is defined as the temperature where the viscosity value corresponds to 10^{12} Pa.s. This point is usually denoted as viscosity glass transition temperature. Adding of 1 at. % of germanium to pure selenium causes a significant shift of T_{12} equal to 6.2 K [8]. The same amount of typically three-fold coordinated arsenic shifts T_{12} by only 4.4 K [38]. And finally, only 2.1 K shift [39] is observed in the case of 5 at. % adding of tellurium into selenium. This relatively small shift is not surprising because both elements are chemically very similar and Se–Te glasses form miscible solid solutions [40]. It is also apparent from Fig. 3 that the data published by Nemilov [8] for Ge_1Se_{99} and Ge_3Se_{97} are well correlated with our measurements, reported in this work. The similarity of viscosities between samples containing 1 and 2 at. % of germanium in low viscosity region of undercooled melt is not rare. This coincidence of viscosity curves for materials with similar compositions, or even their crossing, was observed for example in the case of copper addition to arsenic triselenide [41] or tellurium to pure selenium [39].

As was mentioned in the introduction part, there are no literature data for undercooled melts and glasses of $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98}. On the other hand, Perron et al. [15] published viscosity data of these materials in melt region. These data together with our data are plotted in Fig. 4. The parameters of VFT fits through the whole viscosity intervals are summarized in Table 2. Data for pure selenium [15, 37] are also plotted and fitted for comparison. It is apparent from Table 2 that data are fitted by different form of VFT equation that is mentioned in previous text (Eq. 4). Instead of classical parameters B and T_0, the kinetic fragility m and viscosity glass transition temperature T_{12} is used. This form of VFT was introduced by Mauro and coworkers [34]. Kinetic fragility parameter is here defined according to Angell plot [42] as a slop of $log\eta$ dependence on reduced temperature T_{12}/T close to T_{12}. The reason for rewriting of VFT equation by different parameters is the fact that all three parameters (kinetic fragility, viscosity glass transition temperature and viscosity at infinite temperature) are often used parameters for description and comparison of different glass-forming materials. It should be also mentioned that Mauro et al. in their work [34] also rewrite the other typical viscosity theories which allows easy comparison even between different theories fitted through same experimental data [39].

The viscosity theories introduced by Ojovan [33] and Mauro et al. (MYEGA) [34], were also tested. Nevertheless, both of them fit experimental data with higher error than VFT equation. It is probably caused by the fact that the viscosity dependencies of glass-forming systems studied in this work show non-Arrhenius behavior already in undercooled melt regions. This behavior is typical for selenium and generally for systems with high fragility. Therefore, it is not surprising that $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} show this behavior similar to other glass-forming materials with high selenium content [8, 38, 39]. The VFT equation, which predicts divergence of viscosity dependence at T_0 temperature, can usually better describe experimental viscosities of systems with non-Arrhenius behavior in undercooled melt region if also the melt viscosities are included. The Ojovan equation predicts asymptotic Arrhenius behavior in region of undercooled melt and hence fit through experimental data of $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} show high error. Similarly, MYEGA equation also fits viscosities of studied systems in broad temperature interval with higher error than VFT equation. Moreover, parameters $log\ \eta_0$ of MYEGA fits through experimental and literature data are -2.26 and -2.19 for $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98}, respectively. These values are higher than values of VFT fits (Table 2) and also higher than value -5 predicted by Angell's plot [42] and out of range predicted by Nemilov (-4.5±1) [43]. Therefore, it seems that VFT equation provides a plausible description of experimental data.

5. Conclusion

The penetration and parallel-plate methods were confirmed as appropriate methods for determination of viscosity of glass-forming materials in relatively broad viscosity interval. Thermomechanical analyzer (TMA), which is relatively wide spread instrument, can be used for measuring viscosity by these two methods. The accuracy of measurement is estimated up to 0.05 in logarithmic scale according to measurement of standard NBS glass. Nevertheless, several important aspects of measurement must be fulfilled to keep this accuracy of measurement. Especially, very precise calibration of temperature is needed. The viscosity data measured by penetration and parallel-plate methods for $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} chalcogenides are summarized. The adding of germanium to selenium causes expected shift of viscosity curves to higher temperature region due to the increasing of the structure crosslinking.

6. Acknowledgment

This work was supported by the Czech Science Foundation under project No. 16-10562S and by IGA University of Pardubice under the research project SGS_2017_007.

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Figure captions

Fig. 1: Schematic setup of penetration method (a-hemispherical, b-cylindrical indenters) and parallel-plate method (c).

Fig. 2: Experimental viscosity data of standard material NBS 711 measured by penetration (hemispherical and cylindrical indenters) and parallel-plate methods. The tabulated data for NBS 711 are also depicted (◆). VFT fit through experimental and tabulated data (more details in Discussion section) is used.

Fig. 3: Viscosity logarithm of $Ge_{0.5}Se_{99.5}$ (▲) and Ge_2Se_{98} (●) glass-formers plotted versus reciprocal temperature. Our previously published experimental data [37] for pure selenium (■) and data for Ge_1Se_{99} (△) and Ge_3Se_{97} (○) published by Nemilov [8] are also depicted. The experimental data are fitted by VFT equations.

Fig. 4: Viscosities of $Ge_{0.5}Se_{99.5}$ (▲) and Ge_2Se_{98} (●) glass-formers plotted versus reciprocal temperature in broad viscosity interval. Our previously published experimental data [37] for pure selenium (■) are also depicted. The open symbols represent data for melt region published by Perron et al. [15] (for keeping clarity only each second point is plotted). The data are fitted by VFT equations.

Table 1

Viscosities (Pa.s) of $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} measured by penetration and parallel-plate methods.

T (K)	log η	T (K)	log η
$Ge_{0.5}Se_{99.5}$		Ge_2Se_{98}	
313.0	$12.25^{\bullet}$	304.1	$12.56^{\bullet}$
315.1	$11.70^{\bullet}$	305.7	$12.00^{\bullet}$
315.5	11.53	306.6	$11.81^{\bullet}$
318.1	10.96	307.4	$11.42^{\bullet}$
320.2	10.40	310.8	10.76
322.7	9.99	314.6	$10.10^{\bullet}$
328.2	9.16	318.1	9.53
333.4	8.52	321.4	9.11
333.6	8.44	323.2	8.70
337.9	8.01	324.5	8.46
338.7	7.90	325.0	8.42
345.1	$7.30^{=}$	329.0	8.06
350.1	$6.81^{=}$	333.9	7.53
355.2	$6.33^{=}$	336.4	$7.27^{=}$
359.8	$6.06^{=}$	340.5	$6.99^{=}$
364.5	$5.80^{=}$	345.8	$6.48^{=}$
369.5	$5.43^{=}$	350.9	$6.04^{=}$
374.1	$5.14^{=}$		

Experimental points are marked according to method which was used for their determination; parallel-plate$^{=}$, penetration with hemispherical indenter$^{\bullet}$, penetration with cylindrical indenter (without symbol).
Accuracy of temperature measurement is ± 0.5 °C, accuracy of viscosity measurement is ± 0.05 log units.

Table 2

Parameters of VFT fits through selenium data [37] and $Ge_{0.5}Se_{99.5}$ and Ge_2Se_{98} experimental data from this work combined with data published by Perron et al. [15] (viscosity interval $10^{-1.5}$ – $10^{12.5}$ Pa.s).

	$\log \eta_0$	m	T_{12} [K]
Se	-3.87±0.04	64.3±0.8	301.3±0.2
$Ge_{0.5}Se_{99.5}$	-3.63±0.05	66.2±0.8	305.1±0.2
Ge_2Se_{98}	-3.49±0.07	63.8±1.0	312.5±0.3

Errors correspond only to errors of fitting.

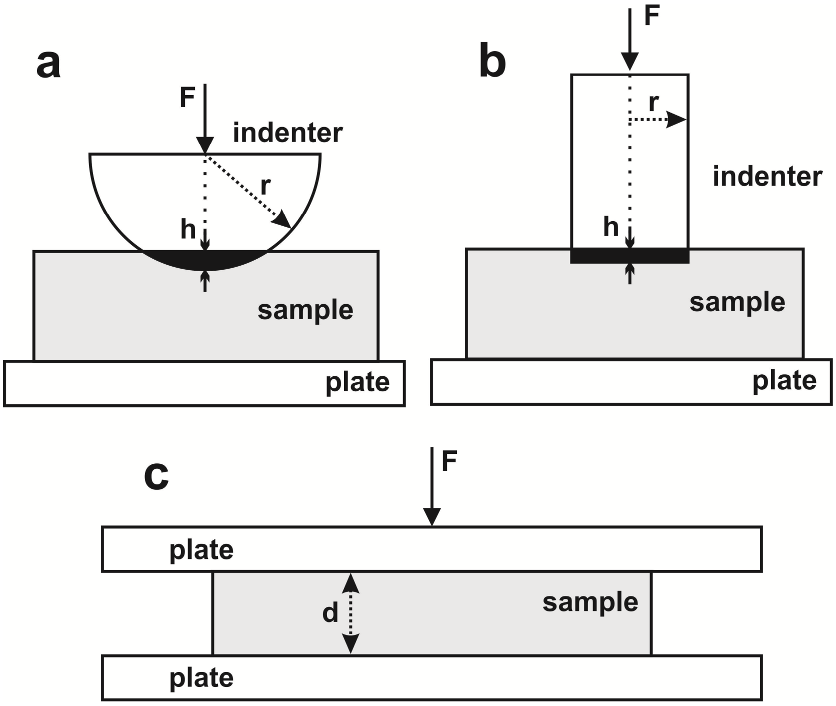

Fig. 1: Schematic setup of penetration method (a-hemispherical, b-cylindrical indenters) and parallel-plate method (c).

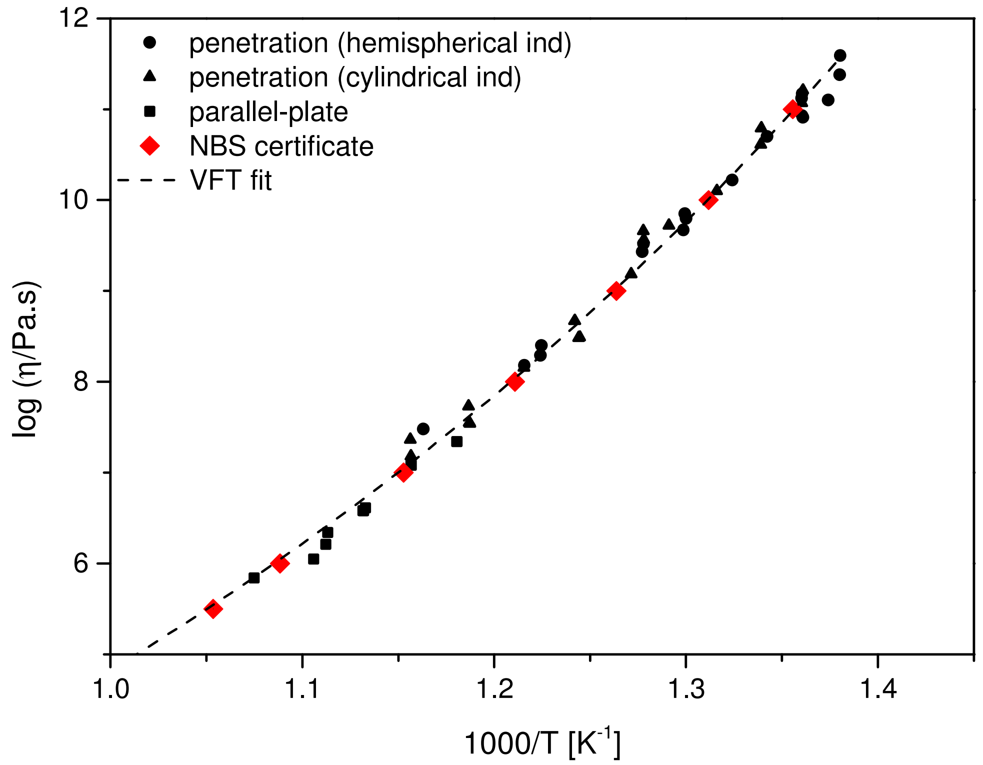

Fig. 2: Experimental viscosity data of standard material NBS 711 measured by penetration (hemispherical and cylindrical indenters) and parallel-plate methods. The tabulated data for NBS 711 are also depicted (◆). VFT fit through experimental and tabulated data (more details in Discussion section) is used.

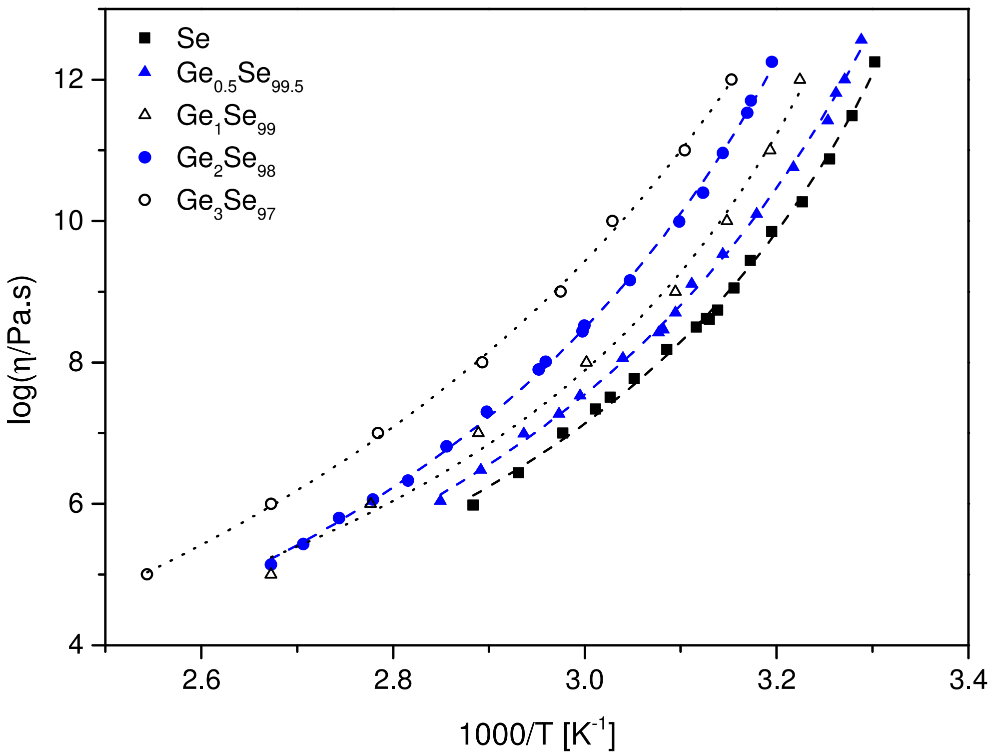

Fig. 3: Viscosity logarithm of $Ge_{0.5}Se_{99.5}$ (▲) and Ge_2Se_{98} (●) glass-formers plotted versus reciprocal temperature. Our previously published experimental data [37] for pure selenium (■) and data for Ge_1Se_{99} (△) and Ge_3Se_{97} (○) published by Nemilov [8] are also depicted. The experimental data are fitted by VFT equations.

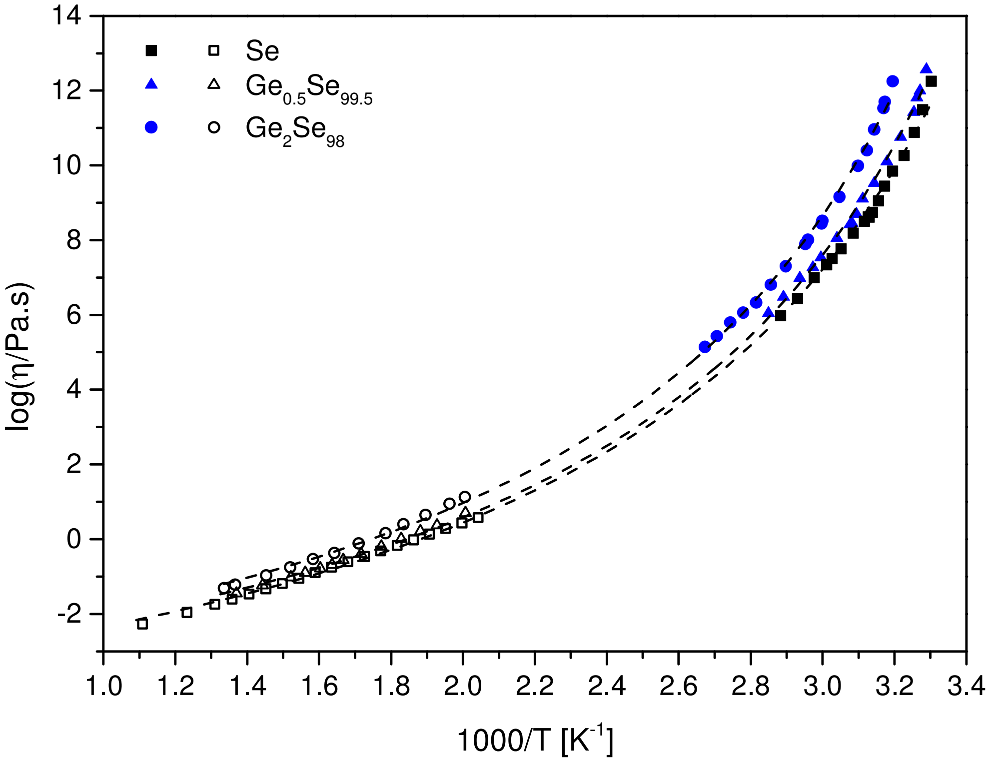

Fig. 4: Viscosities of $Ge_{0.5}Se_{99.5}$ (▲) and Ge_2Se_{98} (●) glass-formers plotted versus reciprocal temperature in broad viscosity interval. Our previously published experimental data [37] for pure selenium (■) are also depicted. The open symbols represent data for melt region published by Perron et al. [15] (for keeping clarity only each second point is plotted). The data are fitted by VFT equations.