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Thermomechanical analysis as a useful tool to study photoinduced changes of the viscous flow of glassy materials

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A modified thermomechanical analyzer is described as an useful tool to study the photoinduced changes in the viscous flow and thermal properties of glassy materials. The device proposed was tested on model chalcogenide glass As_2S_3 using the penetration method. Further, the article discusses and summarizes the effect of the light illumination (at wavelength of 650 nm) on the viscous flow at different temperatures below the glass transition temperature (T_g), and on the thermal behaviour interpreted from dilatometric curves via glass transition temperature and softening temperature.

Keywords: Glass; Thermomechanical analysis; Viscosity; Photoinduced changes

Introduction

The thermomechanical analysis (TMA) is one of the basic approaches of thermal analysis based on monitoring the sample dimension changes during the heat treatment**.** The respective method has also a wide practical applicability in testing of materials. It is commonly used to study the structural relaxation, glass transition, thermal expansion, viscosity behaviour, etc. Knowledge of viscosity behaviour, especially in the case of glass-forming materials, is very important for

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glass processing because it describes the viscous flow of a material. Viscosity is affected by many factors, such as inhomogeneities in glass, structural relaxation, or crystallization processes [1] and also strongly depends on the temperature as described by Angell [2]. In addition to the features listed above, viscosity of some glassy materials can be influenced by illumination. The influence of the light illumination on the viscous flow of chalcogenide glasses has already been investigated by different techniques [3–8]. This photoinduced phenomenon is studied due to the potential application in the preparation of optoelectrical and optical devices, such as optical fibers [3].

Glassy As_2S_3 is one of the widely studied chalcogenide glasses with known thermal properties [9] and well-defined temperature dependence of viscosity [9–11]. This material is also known for its good photosensitivity [3], which is the reason why this type of glass is used in this work – as a model system to study the photoinduced changes.

The aim of this work is to test the eligibility, reproducibility, and thermal stability of viscous flow measurements on the model As_2S_3 glass using modified thermomechanical analyzer with quartz hemispherical indenter (of the optical quality) and to study the effect of the light on viscous flow at different temperatures below the glass transition temperature. The comparison of our data with those obtained using other methods [4,6,8] is also discussed.

Materials and methods

Sample preparation

The As_2S_3 glass was prepared by synthesis from the pure elements (arsenic, purified by annealing in high vacuum at 300 °C to remove arsenic oxide [12]; sulfur, purified using von Wartenberg technique [13]). The adequate amounts of purified elements were weighed (10 g in total) into a clean quartz ampoule. Subsequently, the ampoule was evacuated, sealed, and then placed in a rocking furnace. Firstly, the obtained mixture was heated to 145 °C for 1 hour to melt sulfur. Then, the temperature was increased up to 800 °C. After heat treatment and homogenization for 7 hours, the ampoule was cooled down at air. The as-prepared As_2S_3 glass was annealed at 130 °C for 8 hours to remove stress. The chemical composition of As_2S_3 was controlled by a scanning electron microscope (JSM-5500LV; JEOL, Tokyo, Japan) coupled with X-ray (EDX) analyzer (IXRF System; detector GRESFAM Sirius 10). A plan-parallel thin plates (1 ± 0.1 mm thick) brushed from both sides by alumina powder (with particles size of 5 μm) were used for the viscosity measurements.

Modified thermomechanical analyzer

Thermomechanical analyzer, (TMA CX 03RA-T, R.M.I., Lázně Bohdaneč, Czech Republic), is commonly used to measure the thermal properties of glass-forming materials (glass transition temperature (T_g), softening temperature (T_s), coefficient of thermal expansion (α) or viscosity) by various approaches, such as penetration method. The mentioned instrument is based on the measurement of the sample length changes by differential-capacitance displacement probe detector. The detector is controlled through an electronic system which ensures linearity with deviation lesser than 0.1 %, high sensitivity (0.01 mm resolution), and a low noise (typically 0.02 mm without signal filtering). This instrument is able to measure from ambient temperature up to 800 °C using the heating rates 0.1–10 °C/min. The interval of applied forces is up to 1 N with 1 mN step. Thermomechanical analyzer was calibrated by height standards and by temperature standards (In, Pb, Sn, Zn, and Al). The melting temperatures of each metal were measured with constant force of 10 mN using different heating rates (0.2; 0.5; 1; 2 and 5 °C/min) and detected through the significant decrease of sample height. The melting temperatures were plotted in the dependence of heating rate and extrapolated to 0 °C/min. The accuracy of temperature value during the measurement was ±0.5 °C; the applied force being calibrated by known weight standards.

The above-described classical thermomechanical analyzer was modified to examine photoinduced changes in the viscous flow by the penetration method while maintaining the ability to measure the common thermal properties (e.g. viscosity in equilibrium state (η) and characteristic temperatures); see Fig. 1. Therefore, the classical indenter for penetration method (typically corundum or steel hemisphere) was removed and the optical-quality quartz hemispherical indenter (the radius of hemisphere R = 1.02 mm) made at our department was used in order that the beam from the laser source (attached above the instrument furnace) could pass through the whole optical path. The material of an optical quality quartz rod for a new indenter was intentionally selected to avoid scattering and optical losses of the passed light. The quartz rod was carefully processed by cutting and heat shaping to obtain the final shape of the indenter fulfilling the required conditions for measuring viscosities by the penetration method. This setup enabled simultaneous focusing of the laser beam at the point of penetration on the sample surface. Thermomechanical analyzer modified in this way was then used for both measurements; i.e., common thermal properties (η, T_g and T_s) and the changes in photoinduced viscous flow.

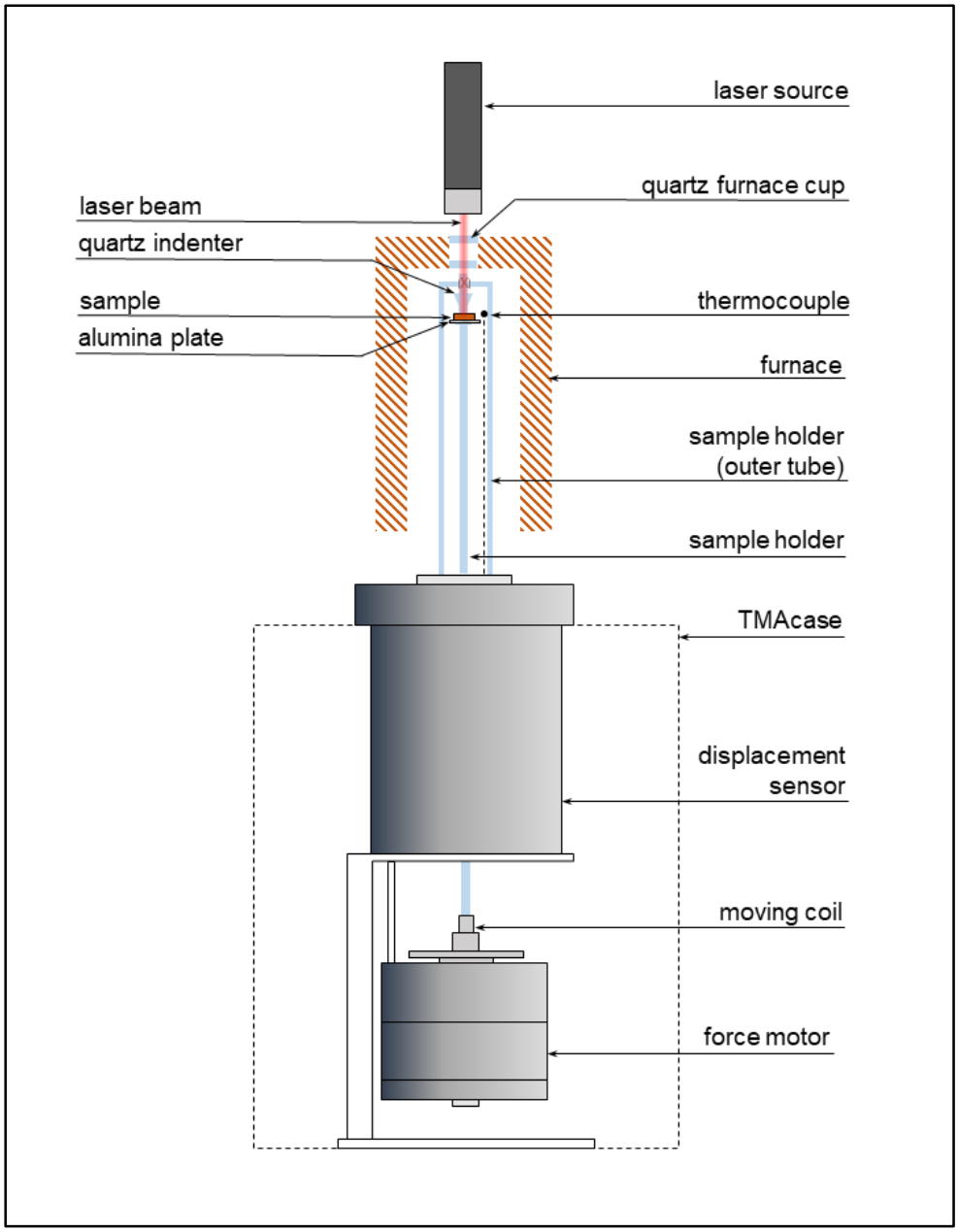

Fig. 1 Schematic outline of the thermomechanical analyzer TMA CX 03RA-T adapted for the study of photoinduced changes on viscous flow

Measurements of viscosity and of photoviscous changes

Both properties (viscosity and photoviscous changes) were studied on the model bulk As_2S_3 glass employing modified thermomechanical analyser and the penetration method based on measuring of penetration of hemisphere indenter with radius R pushed by constant force F into a flat sample of a material. The penetration depth h is calculated from position change of the indenter as a function of time t. The value of η can be determined using an equation which holds for $h << R$ [14,15]:

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

The applicability of this equation is being verified by plotting the dependence of $h^{3/2}$ on t. If the dependence is linear, the equation is applicable. This method was firstly described by Cox [16] and for the hemispherical indenter used it can be used in the viscosity interval from 10^9 to 10^{13} Pa s. This method is absolute and no calibration is needed.

Viscosity measurements were performed in three steps. At first, a flat sample of glass placed in thermomechanical analyzer cell between alumina plate and optically transparent quartz hemispherical indenter was heated at 10 °C/min to the required temperature T using loading force of 1 mN. Then, the sample temperature with the same force was equilibrated for 10 min. In the third step, the force of 500 mN was applied and the h measured for 48–84 hours (depending on the temperature) to attain the value of η in equilibrium state. For verification of the applicability of the modified thermomechanical analyzer and accuracy of viscosity measurements, the viscosity standard commercial NIST SRM 717a [17] was chosen.

In the case of measurements of the photoinduced viscous flow changes, a continuous-wave laser source was used producing the coherent monochromatic beam with wavelength λ = 650 nm (photon energy E_{ph} = 1.91 eV, laser power density F_L = 2.1 W/cm^2). The measurements were performed similarly as in the case of viscosity; however, in the third step, the maximal time was 540 min to keep the same force applied in all measurements when keeping $h << R$ condition.

Dilatometric measurements

The thermomechanical analyzer was designed and modified mainly for measuring of photoinduced changes in glasses. The effect of laser light on the shape of the dilatometric curves, especially on the T_g and T_s values, was examined during intrinsic cycles using a constant applied force F = 10 mN. The rectangular sample of As_2S_3 glass (4 × 4 × 2 mm) with parallel planes was first heated to a temperature of 230 °C, which is above T_g, to erase previous thermal history. In the second step, the sample was cooled to 120 °C at a selected rate q^- (1; 3 or 5 °C/min). In the third step, the sample was immediately reheated to temperature above T_g at the same heating rate at which it was previously cooled. The change of the sample length was accurately recorded as a function of temperature.

Results and discussion

Viscosity of SRM 717a standard glass

The applicability of modified thermomechanical analyzer and also the accuracy of viscosity measurement were tested on viscosity standard glass SRM 717a; the values of this borosilicate glass being certified for a wide temperature range [17]. The temperature dependences of tabulated and experimental data are compared in Fig. 2. The data were fitted Vogel–Fulcher–Tammann (VFT) equation [18–20]:

$$\log \eta = A + \frac{B}{T - T_0} \tag{2}$$

where A, B and T_0 are temperature independent constant for given system. VFT equation for SRM 717a standard is also given in the certificate. It can be seen that our experimental data measured in the temperature range from 530 to 570 °C are in good agreement with the tabulated data and the deviation from the VFT fit is not higher than 0.2 log units. The highest deviation of the experimental data from VFT fit is for viscosity of $10^{9.85}$ Pa s. The reason for this deviation can be the fact that this viscosity value is close to the lower limit for the application of the penetration method employing the hemispherical indenter.

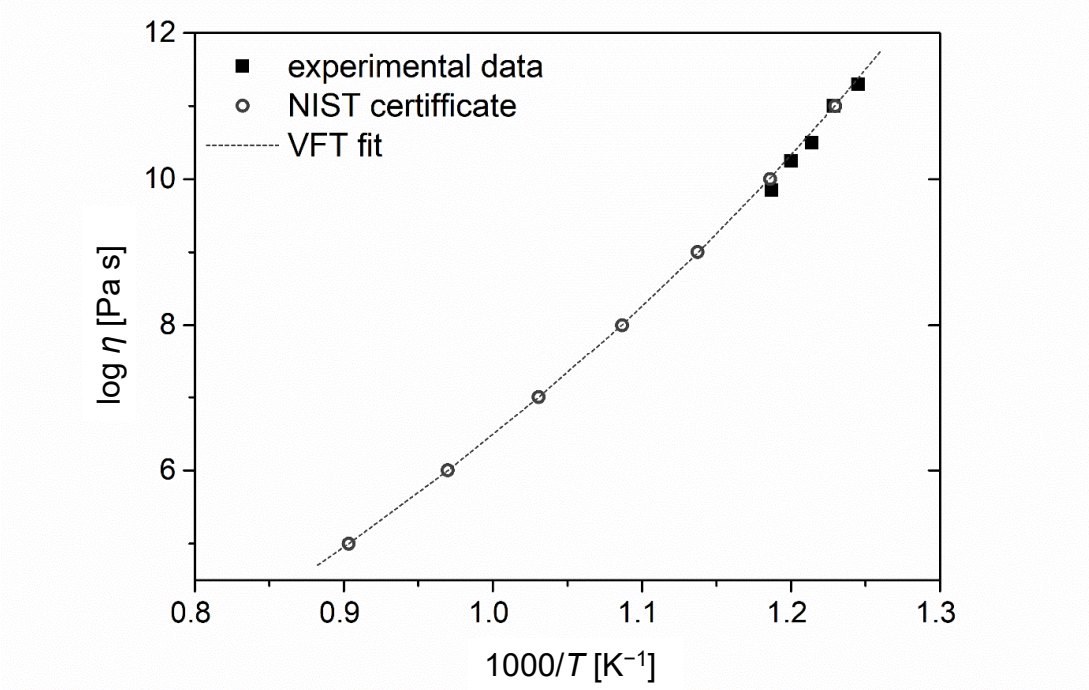

Fig. 2 Viscosity data for viscosity standard SRM 717a: (■) our data measured by penetration method employing modified thermomechanical analyzer and (○) the tabulated data [17] plotted versus reciprocal temperature
The tabulated data are fitted by VFT equation (2)

Viscosity of As_2S_3 glass

The viscosity measurements of glass and undercooled liquid of As_2S_3 were performed using penetration method described above. The temperature dependences of our viscosity data and selected data published previously by Málek [9], Nemilov [10], and Hofírek [11] are summarized in Fig. 3.

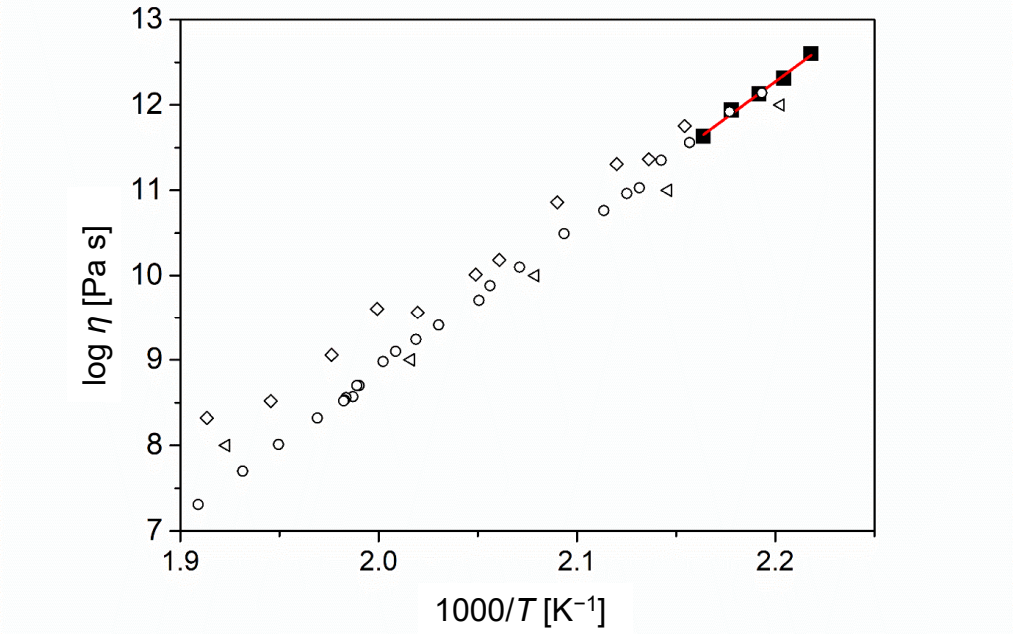

Fig. 3 The temperature dependence of logarithms of viscosity (logη) of A_2S_3: our data (■), Hofírek [11] data (○), Málek [9] data (◇), and Nemilov [10] data (◁)
The solid line corresponds to linear fit of our data.

Our data (full squares) were measured in the region of low temperatures close to the viscosity glass transition temperature T_{12} (the temperature at viscosity 10^{12} Pa s, above this temperature the material is transformed into the undercooled liquid). In contrast to other properties (e.g. enthalpy, sample length, volume), viscosity does not change the slope of its temperature dependence during the glass transition. Our data do not exhibit curvature and, therefore, a value of the apparent activation energy of viscous flow E_η and the viscosity glass transition temperature T_{12} can be determined using Arrhenius-type equation:

$$\log\eta = \log\eta_0 + \frac{E_\eta}{\ln 10\, RT} \tag{3}$$

where η_0 expresses preexponential factor, R is universal gas constant and T corresponds to temperature in K. A value of the apparent activation energy of viscous flow was found to be E_η = 328 ± 17 kJ/mol and the viscosity glass transition temperature was T_{12} = 185 °C. The literature data [1,9–11] show

a relatively wide range of these values ($T_{12} \approx$ 172–189 °C; E_η = 267–386 kJ/mol) depending on the method for viscosity measurements, temperature range used or the different preparation and thermal history. Our data are in good agreement with data published by Hofírek [11] (E_η = 327.7 ± 1.7 kJ/mol, T_{12} = 184.9 ± 0.6 °C) measured by penetration and parallel-plate method in a relatively wide range of viscosities extending slightly above 10^{12} Pa s.

Photoinduced changes on viscous flow of As_2S_3 glass

The photoinduced changes on viscous flow behaviour of As_2S_3 glass (optical band-gap energy E_g^{opt} = 2.4 eV [3]) were studied by penetration method using the optically transparent quartz hemisphere indenter as well. Fig. 4 shows the comparison of typical time dependence of viscosity for non-illuminated and illuminated As_2S_3 glass at T = 178 °C. For illumination, the laser beam emitted at sub-band gap wavelength (λ = 650 nm, F_L = 2.1 W/cm^2) was used. Although the equilibrium value of η was not reached due to a short measurement time (longer time leads to a large indenter penetration depth and the condition $h << R$ would not be fulfilled), the decrease of viscosity of illuminated sample is evident when compared with non-illuminated sample.

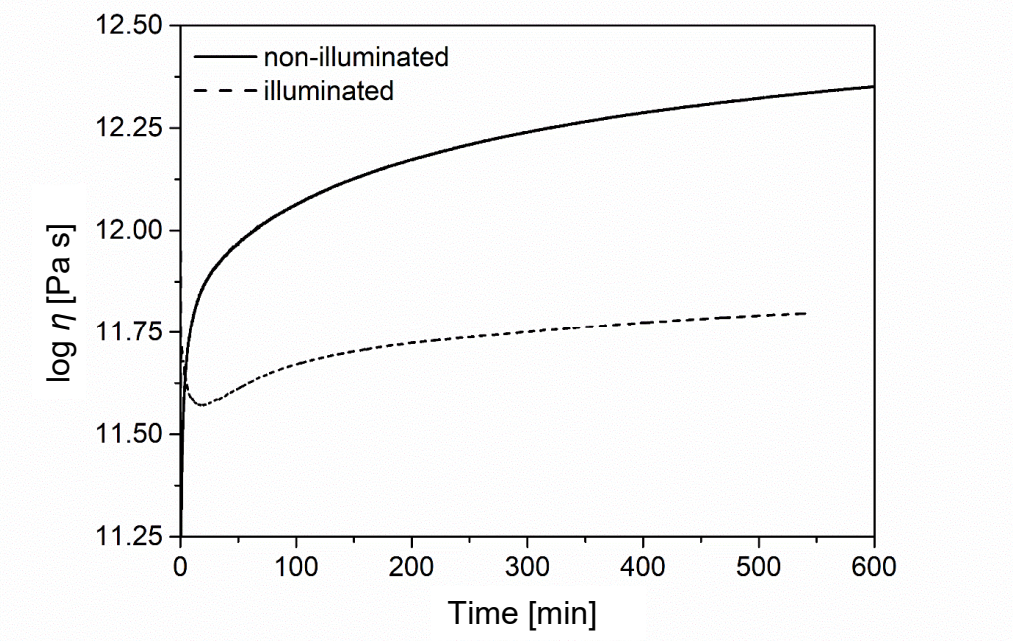

Fig. 4 Comparison of viscosity measurements of non-illuminated and illuminated (λ = 650 nm, F_L = 2.1 W/cm^2) samples of As_2S_3 glass measured at 178 °C

For descriptions of the effect of light on materials instead of η due to the above-mentioned reason, the changes of the penetration depth h for the maximal time 540 min were measured. The Fig. 5 shows a comparison of the time dependence of penetration depth of non-illuminated and illuminated samples for five different temperatures below T_g. It can be seen that the h increases with temperature due to the increasing viscous flow being amplified by illumination. The h values after annealing time 540 min were found to be 12.9–54.6 μm for non-illuminated sample and 29.6–97.3 μm for illuminated sample in the same temperature range. It might seem that the effect of light has increased with increasing temperature, but if we consider, for time 540 min, the ratio between the penetration depth for illuminated and non-illuminated sample $h^{ill}/h^{non\text{-}ill}$ which decreases with temperature from 2.3 to 1.8, we come to the opposite conclusion. It is why we assume that the effect of illumination on the viscous flow decreases with increasing temperature and the observed behaviour appears to be athermal. This finding is consistent with the literature dealing with similar phenomena in various chalcogenide glasses [3,8].

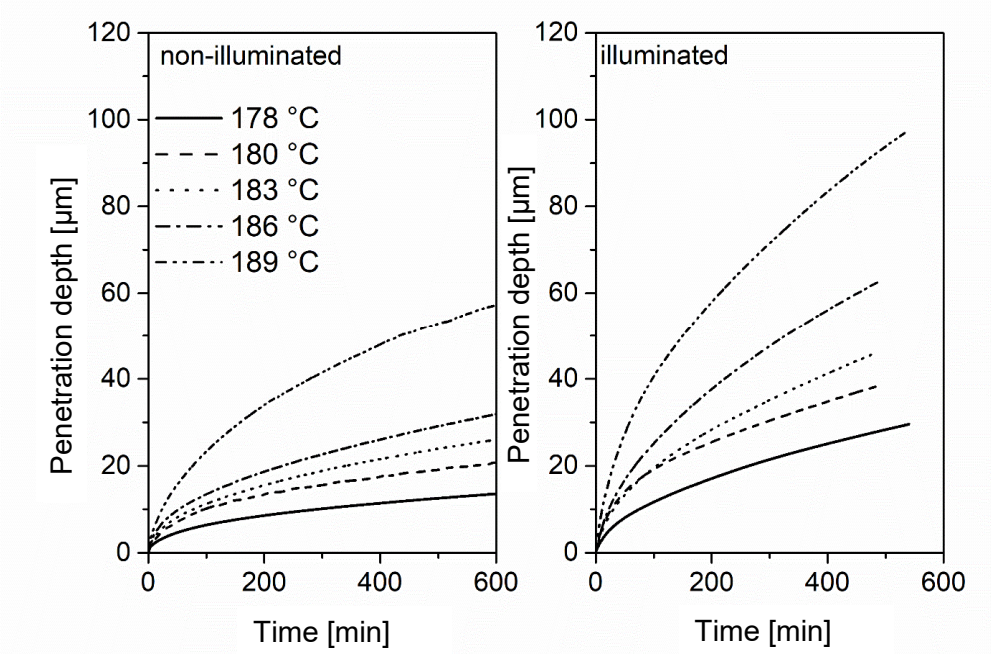

Fig. 5 Time dependence of h of non-illuminated and illuminated ($\lambda = 650$ nm, $F_L = 2.1$ W/cm^2) samples of As_2S_3 glass measured at different temperatures

It should be noted that the above-mentioned photoviscous changes were not observed in conventional oxide glasses with rigid structure, such as borosilicate glass PYREX [3]. It is assumed that these effects can occur only in special photosensitive glasses during the exactly defined conditions (temperature, illumination and mechanical stress); e.g., for As_2S_3 glass at ambient temperature, the photoviscous

changes occur at high laser power density illumination (F_L > 100 W/cm^2) [3] or, in our case, taking place slightly below the glass transition temperature at simultaneous low laser power density 2.1 W/cm^2 and applied force 500 mN.

The observed photoviscous changes are useful mainly for preparation of various microoptical devices (i.e., microlenses, waveguides or modified optical fibers [21,22]).

The role of light on dilatometric measurements

The thermal properties (i.e., T_g and T_s) of rectangular sample of A_2S_3 glass including the role of illumination were studied during intrinsic cycles using TMA. During heating, the length of a glassy sample first slightly increases with temperature. Thermal expansion is caused by the asymmetry of the amplitude of thermal vibration in the glass [23]. During further heating, the material attains the glass transition region, where the structure starts to become unrestrained, the glass turns into undercooled liquid, and the sample is expanding more rapidly. After reaching the softening temperature, the creep caused by the viscous flow exceeds the expansion of a material and the sample begins to deform. The value of T_g was determined as the intersection of extrapolated parts of the dilatometric curve corresponding to glassy and undercooled liquid regions. The T_s value was determined as maximum of dilatometric curve.

The obtained characteristic temperatures for non-illuminated and illuminated A_2S_3 sample are summarized in Fig. 6. It can be seen that there is evident effect of the light illumination on these temperatures is evident for the same heating rates. The values of T_g and T_s of the illuminated samples are lower by approximately 8–9 °C and 4–6 °C, respectively, compared to the values of non-illuminated samples. It seems that T_g is more influenced by illumination than T_s.

This corresponds to the theory (see [3,4,8]) postulating that the effect of photons decreases with the increasing temperature. The decrease of T_g due to the illumination effect was also observed by Tagantsev and Nemilov [4] or by Tanaka and Shimakawa [6].

Although some theories were suggested to explain the observed behaviour — e.g., photoinduced chain breaking —, the proper mechanism is still not clear.

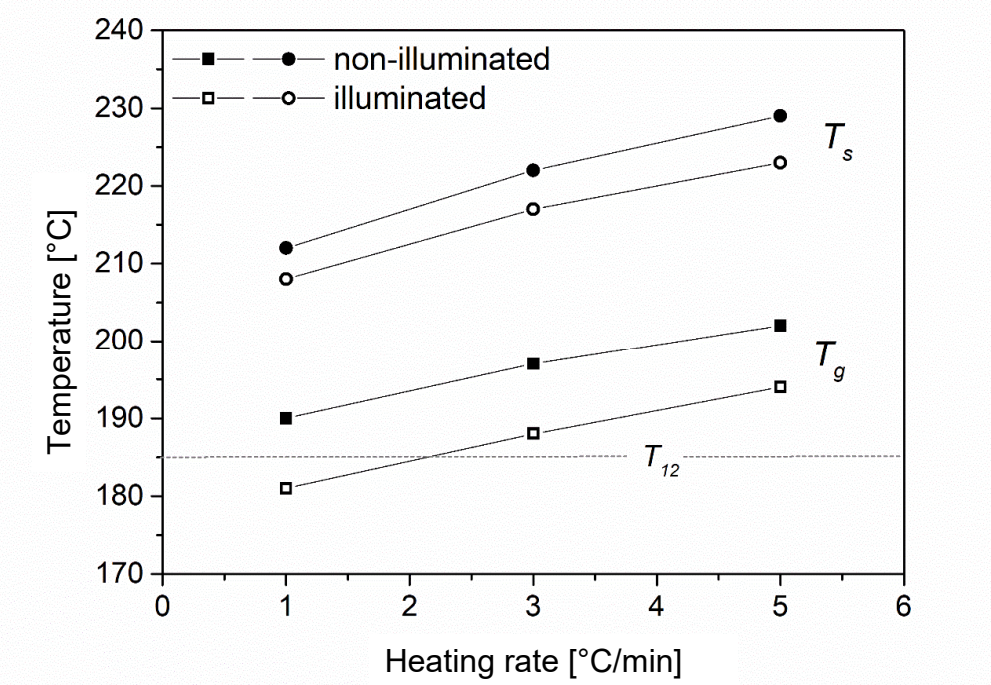

Fig. 6 The change of characteristic temperatures (glass transition temperature T_g and softening temperature T_s) obtained from dilatometric curve for non-illuminated and illuminated As_2S_3 (λ = 650 nm, F_L = 2.1 W/cm^2) as a function of heating rate Dashed line corresponds to value of the viscosity glass transition temperature T_{12} determined from viscosity measurements.

Conclusions

The thermomechanical analyzer was modified to enable the measurements of photoinduced changes on the viscous flow in model bulk glass As_2S_3. Measurements of the equilibrium state viscosity η on the viscosity standard SRM 717a and As_2S_3 bulk glass and their comparison with relevant literature data was verified and confirmed showing that our modified thermomechanical analyzer is suitable for measurements of viscosity and the viscous flow changes induced by illumination.

It has been found that the light illumination of As_2S_3 glass leads to an increase of viscous flow, which is reflected in an increase in the penetration depth of the indenter during viscosity measurements. The effect of illumination was also observed as a shift of the glass transition temperature and the temperature of softening during dilatometric experiments.

Furthermore, it has been ascertained that the effect of light on the viscosity behaviour and the already mentioned thermal properties of model As_2S_3 bulk glass possesses the decrease with the increasing temperature. The mechanism of decrease of the glass transition temperature due to illumination is not still clear and more experiments are needed to explain fully this effect.

The temperature dependence of viscosity and photoinduced viscous flow changes are important parameters for understanding of the mechanism of microlenses, microcraters, and waveguides creation. These objects are the basic components of passive optical elements.

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References

[1] Košťál P., Shánělová J., Málek J.: Viscosity of chalcogenide glass-formers. *International Materials Reviews* **65** (2019) 1–39.
[2] Angell C.A.: Thermodynamic aspects of the glass transition in liquids and plastic crystals. *Pure and Applied Chemistry* **63** (1991) 1387–1392.
[3] Tanaka K.: Photoinduced fluidity in chalcogenide glasses. *Comptes Rendus Chimie* **5** (2002) 805–811.
[4] Tagantsev D., Nemilov S.: Photo viscosity effect in chalcogenide glasses. *Soviet Journal of Glass Physics and Chemistry* (from 1993, *Glass Physics and Chemistry*) **15** (1989) 220–231.
[5] Yannopoulos S.N., Trunov M.L.: Photoplastic effects in chalcogenide glasses: A review. *Physica Status Solidi B* **246** (2009) 1773–1783.
[6] Tanaka K, Shimakawa K.: Mechanism of photoinduced fluidity in chalcogenide glasses: Molecular orbital analyses. *Journal of Non-Crystalline Solids* **481** (2018) 579–584.
[7] Kastrissios D.T., Papatheodorou G.N., Yannopoulos S.N.: Vibrational modes in the athermally photoinduced fluidity regime of glassy As_2S_3. *Physical Review B* **64** (2001) 214203.
[8] Repka M, Frumar M., Hrdlička M.: Photo-induced change of viscosity of glassy selenium below its glass transition temperature. *Journal of Physics and Chemistry of Solids* **68** (2007) 940–942.
[9] Málek J.: Dilatometric study of structural relaxation in arsenic sulfide glass. *Thermochimica Acta* **311** (1998) 183–198.
[10] Nemilov S.V.: The relation between the free energy of activation for viscous flow and the energy of the chemical bonds in glasses. *Soviet Physic-Solid State* **6** (1964) 1075–1078.
[11] Hofírek T.: *Selected physical properties of pure and doped As_2S_3* (in Czech) Diploma thesis, University of Pardubice, Pardubice 2014.
[12] Feltz A., Linke D., Voigt B.: Chalkogenidgläser als infrarotdurchlässige optische Medien, *Zeitschrift für Chemie* **20** (1980) 81–89.
[13] Wartenberg V.: Reinigung von Schwefel von Kohlenstoff, *Zeitschrift für anorganische und allgemeine Chemie* **297** (1958) 226–226.

[14] Exnar P., Hrubá M., Uhlíř J., Voldán J.: Experience with the penetration viscosimeter, *Silikáty* **24** (1980) 169–179.
[15] Dougles R.W., Armstrong.W.L., Edward J.P., Hall D.: A penetration viscometer, *Glass Technology* **6** (1965) 52–55.
[16] Cox S.M.: A method of viscosity measurement in the region 10^8 poises, *Journal of Scientific Instruments* **20** (1943) 113–114.
[17] *Certificate Standard Reference Material 717a*, National Institute of Standards and Technology, Gaithersburg 2018 https://www-s.nist.gov/srmors/certificates/717A.pdf (accessed May 31, 2021).
[18] Vogel H.: Das Temperatur-abhängigkeitsgesetz der Viskosität von Flüssigkeiten, *Physikalische Zeitschrift* **22** (1921) 645–646.
[19] Fulcher G.S.: Analysis of recent measurement of the viscosity of glasses, *Journal of the American Ceramic Society* **8** (1925) 339–355.
[20] Tammann G., Hesse W.: Die Abhängigkeit der Viskosität von der Temperature beu unterkühlten Flüssigkeiten, *Zeitschrift für anorganische und allgemeine Chemie* **156** (1926) 245–247.
[21] Hisakuni H, Tanaka K.: Optical microfabrication of chalcogenide glasses, *Science* **270** (1995) 974–975.
[22] Hisakuni H, Tanaka K.: Giant photoexpansion in As_2S_3 glass, *Applied Physics Letters* **65** (1994) 2925–2927.
[23] Ytes B.: *Thermal expansion*, Plenum Press, New York – London 1972.