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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.

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 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 (5 N purity) were weight into fused silica ampoule. This ampoule was subsequently evacuated (approximately to 10^{-3} Pa) and

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sealed. The rocking furnace was used for melting and homogenization of sample at 800 °C for 20 h. 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 × 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 was 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 h.

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

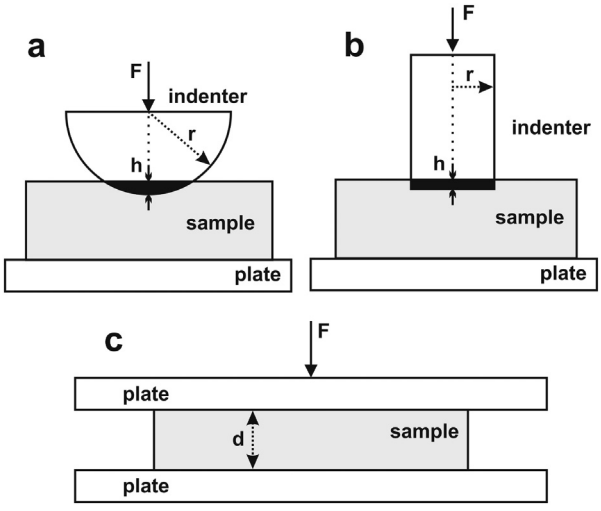

Fig. 1. Schematic setup of penetration method (a-hemispherical, b-cylindrical indenters) and parallel-plate method (c).

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

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 (Eqs. (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