Viscosity measurements of As-Se chalcogenide glass and its use for determination of crystal growth kinetics

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Abstract

Viscosity is a material property which defines how well the material flows. Its knowledge is very important, especially for glassy materials. The crystal growth kinetics is also influenced by viscosity. The diffusion of structural units to the crystal-glass interface is usually very hard or impossible to measure, but it can be replaced by the Stokes-Einstein equation, which correlates diffusion with viscosity. Also, the kinetic crystal growth models are viscosity-dependent, making the knowledge of rheological properties essential (1,2). Our study group, the Málek Research Group, have been interested in the viscosity measurement for a long time, and we've been trying to describe the viscosity of various noncrystalline materials in a broad range of temperatures, from the melted material and undercooled melts to amorphous glass. We've been using many different experimental techniques to achieve that, some of which are introduced in the presented study. The use of these techniques will be demonstrated on an As-Se glassy system.

The first method of viscosity measurement used to study the above-mentioned glass is the thermomechanical analysis (TMA). In this method, the material is being isothermally deformed by force with different setups. The first setup uses different kinds of indenters, where the penetration depth is measured, and from the difference in the height of the measuring probe in time, the viscosity value is calculated. The most used indenters have the shape of a hemisphere, which is suitable for viscosities in a range of 109 to 1013 Pa·s, and a cylindrical shape, which is ideal for a range of 107 to 1011 Pa·s. The parallel plates are another setup used for lower viscosities, mostly in a range of 105 to 107,5 Pa·s. It is performed by pressing a cylindrically shaped sample between two corundum plates, and the value of viscosity is determined from the change in the sample's height (3). All three of the above-elaborated setups with the proper formulas used to calculate viscosity (h) can be seen in Figure 1.

Another method that can be used to measure viscosity is nanoindentation. It is comparable with TMA in a similar execution since this method also uses an indenter, which penetrates the surface of the sample, and the viscosity is calculated from the depth of the indent. The main difference is that the penetration depth is much smaller compared to the TMA, being around tens of nanometres, which makes this method suitable even for measuring samples

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in the form of thin film. The formula to calculate viscosity from the nanoindentation experiment is then expressed in Figure 2 (5,6):

The final method used for viscosity measurement mentioned in this study is the Pressure-assisted melt-filling technique (PAMFT). This method is different from the previous ones because it measures the viscosity in melts. The sample needs to be in the form of a fibre, which is then put into a capillary of similar inner diameter. This capillary is then spliced with another capillary with a much smaller inner diameter, as is shown in Figure 3. This setup is heated above the melting temperature, and the melted sample is pushed from the larger to the smaller capillary with an inert gas. The distance the melt has flown is recorded in time. The experimental setup is shown in Figure 3, with the formula used to evaluate viscosity. This method is a promising new approach for measuring chalcogenide glasses because of their high volatility and corrosivity. Another advantage is using very small amounts of material (less than 0,1 mg). This method's resulting viscosities ranged from 10-1 to 102 Pa·s, but even smaller values could be reached (7,8).

Multiparametric phenomenological models express the temperature dependence of viscosity. One of the simplest models is the Arrhenius-type equation, which is shown in Figure 4 equation (a). Since the logarithmic form of this equation is linear, it is useful only for describing a short temperature range of viscosity data or for materials with low fragility. However, this model is not very useful for most materials (7). The Vogel-Fulcher-Tammann (VFT) equation (9), shown in Figure 4 equation (b), is more suitable for rheologically complex materials. The three-parameters model can describe material behaviour in a more detailed way. One of those parameters is the fragility (m) mentioned above, which is visualised by the curvature of the fitted model. Figure 4 equation (c) is the transcription of the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation (10), described by three parameters and more suitable for semi-fragile materials. The latter model is also used to describe the viscosity data of As20Se80, shown in Figure 4, which were measured by all three above-mentioned experimental techniques (4).

The three mentioned viscosity measurement techniques will be shown in the poster that will be presented at the ICG Spring School 2024. The results of these measurements are demonstrated on AsxSe100-x chalcogenide glass of x = 5, 10, 15, and 20 compositions together with the viscosity model, which best describes their behaviour.

Acknowledgement:

This study was supported by the Czech Science Foundation under project number 24-10480S, the Internal Grant Agency of the University of Pardubice under grant number SGS_2024_007, and the Selected Research Teams program of the University of Pardubice.

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Keywords: Viscosity, Glass, Kinetics, Chalcogenide