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Analysis of crystal growth and viscosity in Ge-Sb-Se-Te undercooled melts

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ABSTRACT

A comprehensive analysis on crystal growth and viscosity is presented for the $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) undercooled melts in this article. Temperature dependence of the measured viscosities ($10^{7.5}$ - $10^{12.5}$ Pa·s) can be described by a simple exponential Arrhenius type equation in the relatively narrow temperature region in which the measurements were performed. Fragility of the measured materials are all roughly equal to 43, which means that these materials belong to the so called "intermediate" liquids (lying in the middle between strong and fragile liquids) and cannot be described by simple Arrhenius type equation if the temperature region is expanded from glass transition to melting, which is important for description of crystal growth. Therefore, MYEGA equation is used to extrapolate the viscosity data into the temperature region of studied crystal growth. Nucleation and crystal growth started on a surface of studied samples. The isothermal growth rate of the formed surface crystalline layer was measured at various temperatures. Analysis of the growth data revealed a crystal growth driven by liquid-crystal interface kinetics. Therefore, the standard crystal growth models were used for description of crystal growth rates in the studied systems.

Keywords: crystal growth, viscosity, chalcogenide glass, Ge-Sb-Se-Te

INTRODUCTION

Amorphous chalcogenides (S, Se, Te) and their binary and multicomponent alloys are very interesting materials with wide practical applications. Their transparency in near-, middle- and far-infrared region and their high nonlinearities make the chalcogenide glasses use as active and passive elements in optics [1, 2], telecommunication, thermal imaging and nonlinear light generation [3-5]. Rapid and reversible crystallization observed in some chalcogenide systems is fundamental for using these materials in non-volatile memories [6-8].

The mentioned applications of chalcogenide glass-forming materials would have not be found without knowledge of fundamental properties, as well as, processes taking place in these interesting materials. The following article is focused on viscosity and crystal growth in chalcogenide undercooled melts. Viscosity is very important physical property of the glassy materials not only for fabrication and processing of the glassy materials, but also viscous flow influences kinetic processes taking place in the amorphous materials, such as structural relaxation [9, 10] and crystallization [11-14]. During the crystallization, transport of the structural units to the crystal-liquid interface is driven by diffusivity (D_f) which can be substituted by viscosity (η) via the well-known Stokes-Einstein relation ($D_f \approx \eta^{-1}$). The temperature dependence of viscosity is then used for description of the kinetic barrier in crystal growth models [15-17]. Proper description of crystal growth rates and extrapolation of the growth rates in wide temperature region is then necessary for a better understanding of the crystallization process in glasses and undercooled melts. The knowledge and possibility to predict the crystal growth behavior in wide temperature range also provides an effective information that can help to prevent or control the amorphous-to-crystalline transformation with respect to the possible usage of the material.

In this article, we present a comprehensive study focused on crystal growth, viscosity and melting in chosen Ge-Sb-Se-Te glassy materials. This system can be of interest as some connection between the Ge-Sb-Te and Ge-Sb-Se systems. The Ge-Sb-Te materials possesses a very fast amorphous-to-crystalline transformation that has found use in optical data-recordings and in electrical memories [7,

18, 19]. On the other hand, Ge-Sb-Se amorphous materials are known for their high thermal stability, low transmission loss and high transparency in infrared region [20-25]. The ternary Ge-Sb-Se-Te system offers interesting opportunities in finding new high-tech materials, which have better thermal stability than the Ge-Se-Te glasses, and also possess faster amorphous-to-crystalline transformation than Ge-Sb-Se materials. Some studies on glass-forming ability [26], thermal properties [27, 28], molar volume and elastic properties [29], and overall crystallization process [30-32] are cited in the literature. Here we focus on $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) bulk materials. We discuss the viscosity behavior and its extrapolation to the crystal growth region based on our previous experience and knowledge. The viscosity is used for description of the crystal growth data using standard crystal growth models with respect to the possible decoupling between kinetic part of the crystal growth rates and viscosities.

EXPERIMENTAL

$Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) bulk glasses were prepared by conventional melt-quench method. Synthesis from appropriate amount of pure elements (5N, HiChem, s.r.o., Prague) in evacuated ($2 \cdot 10^{-3}$ Pa) and sealed silica-glass ampules was performed in a rocking furnace at 800 °C for 20 h. After the synthesis, the ampule was quickly cooled down in iced water. Amorphous nature of the prepared bulk glasses and also crystalline phase after crystal growth measurements were verified by X-ray diffraction analysis (XRD; Bruker AXS X-ray diffractometer D8 Advance equipped with a scintillation counter, utilizing CuK_α radiation - 40 kV, 30 mA). Samples were scanned over scattering angles, 2θ from 5° to 70° at the scanning rate 0.03 °/min.

Melting process and overall crystallization was followed by differential scanning calorimeter (DSC; SensysEvo DSC, Setaram co.). Bulk samples (30 – 50 mg) were placed into open silica ampules and heated up to 650 °C. Heat flow was calibrated using the Joule effect method. Pure Zn (4N, HiChem co., Prague, CZ) was used to verify calibration of heat flow and temperature.

The viscosity behavior of prepared materials were studied by penetration method using thermomechanical analyzer, TMA CX 03 (RMI, Czech Republic). Penetration method is based on measuring a penetration rate of an indenter which is isothermally pushed into a sample applying a constant force [33]. Two different shapes of indenters were used, a corundum hemispherical indenter (3.98 mm in diameter) and two stainless steel cylindrical indenters (1 and 2 mm in diameter). Bulk samples, approximately $6 \times 6 \times 2.5$ mm^3 in size, were cut from glassy samples and ground by corundum abrasive powder before the measurements. The temperature was calibrated on melting points of pure metals (Ga, In, Sn, Pb, Zn, Al). More details about the instrument, calibration, methodology, experimental arrangement and errors can be found in the work of Koštál et al. [34].

Direct measurements of crystal growth were performed by an optical microscope (Olympus BX51 equipped with camera DP72 and infrared camera XM10; in the reflection mode). Samples were previously heat treated in a computer-controlled furnace at selected temperatures (temperature stability ± 0.5 °C) for different times. After the heat treatment, the samples were sectioned to measure thickness of the surface crystalline layer.

RESULTS

Crystal growth

Crystal growth in Ge$_2$Sb$_2$Se$_{5-x}$Te$_x$ (x = 0.5 and 1) undercooled melts was studied in the temperature range of 260 – 340 °C. The bulk samples were treated at a selected temperature for a certain amount of time and then the formed crystals were observed using microscopy. Typical crystals formed in the studied samples are shown in Fig. 1. Both studied compositions (x = 0.5 and 1) revealed the same crystal morphology. The detailed photographs (Figs. 1a and 1e) of the formed crystals show, that the crystals grew from a one single nucleus and the nuclei were randomly distributed on surface of the samples (Figs. 1b and 1f). The crystal evinced dendritic growth forming hemispherical particles (Figs. 1a,c and 1e,g). After a certain time, the hemispherical crystals collided with the others and form a

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compact crystalline layer (Figs. 1b,d and 1f,h). Then, the layer proceeded with growing from the surface to the core of the samples. The thickness of the crystalline layer was measured as a function of heat-treatment time. To get an appropriate value of the surface layer thickness, the layer was measured at several positions in a sample as is shown in insets of Fig. 2, and a mean value was calculated with corresponding errors. Linear evolution of crystalline thickness with preheating time (Fig. 2) provides an information about crystal growth rate at a chosen temperature. Table 1 summarizes crystal growth rates at different temperatures found for the studied chalcogenide materials.

The measurements and evaluation of crystal growth rates were performed in a relatively narrow temperature region. In such case, the crystal growth rate (u) as a function of temperature (T) can be described by simple exponential behavior and activation energy of crystal growth (E_G) can be found. Fig. 3 shows the simple exponential behavior of crystal growth rate on temperature resulting in a linear dependence of ln u vs. 1/T. Slopes of these dependences correspond to E_G/R, where R is the universal gas constant. The activation energies were found to be 316 ± 9 kJ/mol and 326 ± 13 kJ/mol for compositions x = 0.5 and 1, respectively.

Viscosity

The viscosities of $Ge_2Sb_2Se_{5-x}Te_x$ bulk samples (x = 0.5 and 1) were measured by penetration viscometry in undercooled melt and glass regions. The experimental data are summarized in Table 2 and plotted in Fig. 3. Two different shapes of indenters were used. The hemispherical and two different sizes of cylindrical indenters provide consistent viscosity results that show Arrhenius type temperature dependence described by simple exponential equation:

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \qquad (1)$$

This simple equation, which is represented by a straight line in coordinates of Fig. 3, contains two empirical parameters: apparent activation energy of viscous flow (E_η) and preexponetial factor (η_0). Arrhenius type equation can be also rewritten to a form containing two other parameters, kinetic fragility (m) and T_{12} corresponding to a temperature at which viscosity value reaches 10^{12} Pa·s [35].

This transformation is beneficial because these two parameters are often calculated from Arrhenius fits and they are used for a description of experimental viscosity data. Kinetic fragility (m), also known as steepness index, is defined according to normalized Arrhenius plot (better known as Angell plot) [36] as a slope of the viscosity dependence on reduced temperature (T_{12}/T) in the vicinity of T_{12}:

$$m = \left[\frac{d \log \eta}{d\,(T_{12}/T)}\right]_{T=T_{12}} = \frac{E_\eta}{RT_{12}\ln 10} \quad (2)$$

T_{12} is usually denoted as viscosity glass transition temperature. The value 10^{12} Pa·s is generally accepted convention. All the mentioned parameters (E_η, m and T_{12}) were evaluated from the experimental viscosity data and are summarized in Table 3 together with previously found parameters for composition $Ge_2Sb_2Se_5$, published by Barták et al. [37].

Thermal behavior followed by DSC

The thermal behavior of the studied $Ge_2Sb_2Se_{5-x}Te_x$ glasses was followed by differential scanning calorimetry (DSC), especially to determine melting parameters which are important for the crystal growth analysis. The DSC curves of measured samples are shown in Fig. 4 for amorphous and fully crystallized samples. The DSC experiments were performed at heating rate of 5 °C/min. The Fig. 4 shows glass transition at 225 – 235 °C, followed by crystallization with temperatures of peak maxima at 330 °C and 320 °C for compositions x = 0.5 and 1, respectively. With continuing heating, the material starts to melt at approximately 460 °C for x = 0.5 and 480 °C for x = 1. The melting process of the studied materials is quit complex, followed probably by recrystallization and evaporation of the material. In such complex process, only the onset of melting (T_m) could be determined. The onset of melting was evaluated from DSC measurements on both amorphous and fully crystallized samples. The temperatures of melting for both studied compositions were determined from several DSC scans and were found to be T_m = 457.3 ± 1.6 °C and 493.4 ± 2.2 °C for compositions x = 0.5 and 1, respectively. The crystallization enthalpies (ΔH_c) were also determined for the further analysis: ΔH_c = 2.9 ± 0.3 kJ/mol for x = 0.5 and 3.34 ± 0.14 kJ/mol for x = 1.

DISCUSSION

Temperature dependence of viscosity

The temperature ranges where the viscosities were determined are 225 – 285 °C for x = 0.5 and 215 – 270 °C for x = 1 in the $Ge_2Sb_2Se_{5-x}Te_x$ glasses and undercooled melts. These temperature ranges correspond approximately to the viscosity range log (η/Pa·s) 7.5 – 12.5. Measurement of higher viscosities is complicated due to an extremely long times of measurements which the materials need to reach the equilibrium state. Measuring lower viscosity values is, on the other hand, complicated due to the beginning of crystallization process. Growing crystals strongly influence the flow of sample and the correct viscosity value is not measurable.

Important parameters of the viscous flow were found from the experimental data and are listed in Table 3. The data are compared with previously published data on viscosity in $Ge_2Sb_2Se_5$ glass and undercooled melt published by Barták et al. [37]. According to the Table 3, the T_{12} temperature decreases with tellurium content in the $Ge_2Sb_2Se_{5-x}Te_x$ system. This is in a good agreement with decrease of glass forming temperature (T_g) followed by DSC in the work of Svoboda et al. [30]. Similar behavior corresponds to a change of activation energies of viscous flow with tellurium content in the $Ge_2Sb_2Se_{5-x}Te_x$ system. The E_η is sometime identified with an activation energy of structural relaxation (Δh^*) [10]. Svoboda et al. [30] estimated the values of Δh^* in the $Ge_2Sb_2Se_{5-x}Te_x$ glasses from constant heating rate cycles using a methodology based on a shift of temperature corresponding to the maximum of the relaxation peak with the applied heating rate. The activation energies of viscous flow and structural relaxation are compared in Table 3. However, in this particular case, the dependence of E_η on tellurium content reveal an opposite trend than Δh^* and their absolute values differ more with addition of tellurium. The last parameter evaluated from the viscosity data is kinetic fragility (*m*). The fragilities (Table 3) found in the studied $Ge_2Sb_2Se_{5-x}Te_x$ system are independent on tellurium content and their values were obtained to be close to 43. It means that the viscosity dependencies for these compositions lie approximately in the middle between two fragility extremes. In such a case, these

glass-forming materials can be called "intermediate" from the kinetic fragility point of view. The "intermediate" liquids typically exhibit the simple Arrhenius behavior of viscosity in the undercooled melt region, relatively close to T_g. On the other hand, their viscosity behavior in a broad temperature interval, including a region of melt, cannot be described by such a simple equation, and an equation with three or more parameters has to be used.

Viscosity data is important for analysis and description of crystal growth in the studied materials. Such analysis requires description of viscous flow in wide temperature range, usually from glass transition to melting. The measured viscosity values exhibit Arrhenius type behavior but due to the "intermediate" fragility behavior of studied systems, the simple extrapolation by use of the Arrhenius equation is not possible. This approach leads to obtain unrealistic viscosity values because "non-strong" systems exhibit non-Arrhenius behavior in a broad temperature range. The large extrapolation of viscosity into the immeasurable region by use of the Arrhenius type equation can hence cause the distortion of estimated viscosity values. Definitely, the best way to obtain reasonable viscosity data is an interpolation between measurable regions of undercooled melt and melt. Unfortunately, melt viscosities for both studied compositions have not been measured and published yet. Generally, there is a lack of viscosity data for chalcogenide melts in the literature. There are several reasons for that but the main problems are chalcogenide melts themselves. They are highly chemical aggressive and exhibit strong evaporation tendency which really complicate the own melt-viscosity measurements. If the melt viscosities are not available, there is another way how to obtain at least a good estimation of viscosity data. We described this procedure in our previous work [38]. The procedure is based on Angell plot and an assumption that all viscosity dependencies end at 10^{-5} Pa·s for the infinite temperature. As we discussed earlier [38], this is definitely a simplification of viscosity behavior of glass-forming liquids (above melting point). Nevertheless, according to our opinion and experiences, this is the reasonable way to extrapolate viscosity data if melt viscosities are unknown. The different viscosity equations were tested in our work submitted for publishing [39]. Well-described chalcogenide amorphous materials (As_2S_3, As_2Se_3, Se) with measured viscosities in melt region were fitted by VFT [40-42] (Vogel-

Fulcher-Tammann), MYEGA [43] (Mauro-Yue-Ellison-Gupta-Allan) and Ojovan [44] equations. The Ojovan equation is not suitable for any extrapolation with infinite temperature limit fixed in just one point. This equation is unique in shape and contains four or even five parameters. The comparison between VFT and MYEGA equations showed that for "intermediate" liquids the MYEGA equation is more suitable than the VFT. Hence, we used the MYEGA equation for our extrapolation:

$$\log \eta = \log \eta_0 + \frac{B}{T}\exp\left(\frac{C}{T}\right) \qquad (3)$$

This equation contains three parameters (η_0, B, C). Fig. 3 shows measured experimental data for the studied system and extrapolated Arrhenius and MYEGA (with fixed viscosity value at infinite temperature) fits through them. The significant differences between viscosity data estimated by both equations are apparent. Values of the found parameters of the MYEGA equation for the studied samples are listed in Table 4.

Crystal growth kinetics

In the results part it was shown, that the crystal growth in the $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) undercooled melts started from randomly distributed nuclei on the surface of the studied bulk samples. The crystals grew as hemispherical particles formed from intertwined dendrites until the crystals reached one another. After that, the crystals formed a compact crystalline layer, which continued with the growth from the surface to the core of the samples. The found activation energies of crystal growth (E_G = 316 ± 9 kJ/mol and 326 ± 13 kJ/mol for x = 0.5 and 1, respectively) correspond well with activation energy of crystal growth (E_G = 340 ± 5 kJ/mol) found for tellurium-undoped $Ge_2Sb_2Se_5$ material [37]. It seems that the E_G stays more or less constant with the tellurium content in the $Ge_2Sb_2Se_{5-x}Te_x$, even when the crystal growth rates are shifted to higher values with increasing tellurium content (Fig. 3). This phenomenon also corresponds to the shift of DSC crystallization peaks toward lower temperature with increasing amount of tellurium in the samples [30, 45, 46]. The activation energies of overall crystallization process found by DSC [30] in Te-doped $Ge_2Sb_2Se_{5-x}Te_x$ (E_A = 335 ± 16 kJ/mol and E_A = 323 ± 20 kJ/mol for x = 0.5 and x = 1, respectively) are close to those found from crystal growth data. This

similarity can mean that the crystallization process is driven mainly by the crystal growth and the nucleation is negligible in the corresponding temperature region.

Description of crystal growth rates in wide temperature region, usually from T_g up to T_m, is important for processing and utilizing of amorphous materials. The above-described surface crystalline layer formed in $Ge_2Sb_2Se_{5-x}Te_x$ undercooled melts grew linearly in time (Fig. 2) at isothermal conditions. This behavior is typical for crystal growth driven by the liquid-crystal interface kinetics. There are three standard growth models (screw dislocation growth – SDG, normal growth – NG, and 2D surface nucleation growth – 2DG) used for description of crystal growth driven by the liquid-crystal interface kinetics [16, 17]. Jackson et al. [15] proposed a simple way to test the obtained growth data to find an appropriate growth model. The estimation is based on a change of number of active places on the liquid-crystal interface with undercooling of the system ($\Delta T = T_m - T$). The number of active sites on the liquid-crystal interface can be effectively expressed by reduced crystal growth rate (U_R):

$$U_R = \frac{u \cdot \eta}{1 - \exp(-\Delta G / RT)} \qquad (4)$$

Where ΔG is difference in Gibbs free energy between undercooled melt and crystalline phase. In our previous works [11, 37, 38], we showed that the simple Turnbull's approximation ($\Delta G = \Delta H_m \cdot \Delta T / T$) [47] can replace the temperature dependence of ΔG with knowledge of enthalpy of melting (ΔH_m) and temperature of melting (T_m). The melting process in the studied system is shown in the results part (Fig. 4). Obviously, this system features a complex melting process, which makes the evaluation of melting enthalpy impossible. Therefore, we decided to use the crystallization enthalpy instead of the melting one. The same assumption was also made in works dealing with the crystal growth in Ge-Sb-Se system [37, 38]. The calculated dependence of U_R on undercooling (ΔT) is shown in Fig. 5. The dependence shows no trend of the calculated data with respect to their error, which is shown by one point for illustrative purposes. Such diagram (Fig. 5) might suggest no dependence of U_R on ΔT, which would propose a normal crystal growth (NG) model. Nevertheless, it is better to test also the screw dislocation growth (SDG) model, which is based on a lattice distortion. Usage of the SDG model can be

justified by crystal growth starting from the surface of the samples, which can be considered as the largest distortion in the material.

The crystal growth models (NG and SDG) can be expressed as [16, 17]:

$$u = f \cdot \frac{k_B T}{3\pi a_0^2 \eta^{\xi}} \left[1 - exp\left(-\frac{\Delta G}{RT} \right) \right] \qquad (5)$$

Where f represents a temperature dependence of number of active places on the liquid-crystal interface and is equal to 1 for NG model and for SDG model $f = \Delta T / 2\pi T_m$. k_B stands for Boltzmann constant and a_0 corresponds to a parameter of the models, also associated with interatomic distance in the interface layer or hopping distance. Parameter ξ expresses decoupling of crystal growth rate and viscosity [48]. The standard growth models are based on an assumption, that the own transport of the structural units to the liquid-crystal interface is driven by self-diffusion, which can be substituted by inverse viscosity according to the Stokes-Einstein-Eyring relation [49]. Nevertheless, in recent studies on crystal growth [13, 37, 38, 48, 50-54] a significant decoupling of crystal growth rate and viscosity occurred, therefore, the standard crystal growth models were corrected to the decoupling phenomenon by including the decoupling parameter ξ into the standard crystal growth models (Eq. 5). On behalf of this experience, the possible decoupling of crystal growth rate and viscosity was tested using a simple proportionality between kinetic part of crystal growth rate ($u_{kin} = u / [1-exp(-\Delta G/RT)]$) and viscosity ($u_{kin} \approx \eta^{-\xi}$) proposed by Ediger et al. [48]. The linearized dependence of log u_{kin} on log η is plotted in Fig. 6. The slopes of the linear dependences give us directly values of the parameter ξ. The evaluated parameters are practically equal to unity ($\xi = 1.00 \pm 0.02$ for x = 0.5, and $\xi = 1.09 \pm 0.05$ for x = 1), which means that the Stokes-Einstein-Eyring relation holds for the whole measured temperature region and the standard growth models can be applied without any corrections ($\xi = 1$ in Eq. 5).

The above-mentioned analysis on the reduced crystal growth rate (Fig. 5) shows some unconvincing predictions of the NG model for description of the experimental crystal growth rate data in the $Ge_2Sb_2Se_{5-x}Te_x$ undercooled melts. Therefore, also the SDG model is applied to the experimental data. Both models were calculated by the Eq. 5 with the parameter $\xi = 1$. Both used growth models are in a

good agreement with the experimental data (inset of Fig. 7). The models deviate from each other at higher temperatures. Nevertheless, without the growth data obtained at high temperature, especially near the melting point, it is not possible to distinguish, which model is more suitable for extrapolation of the crystal growth data towards high temperature.

Both the models (NG and SDG) include only one fitting parameter a_0 (Eq. 5). The fitted parameters are listed in Table 5. The values of the parameters a_0 are comparable with those found in Ge-Sb-Se bulk materials [37, 38]. The a_0 parameter has several meanings [16, 17, 55], which are connected to the size of structural units and to the liquid-crystal interface. The a_0 is usually described as a jump distance, unit distance advanced by the interface or characteristic size of the structural units at the interface. If we assign the a_0 parameter to a size of structural units at the liquid-crystal interface, the size can be roughly estimated from molar volume (V_M) and Avogadro's constant (N_A): $a_0 = (V_M/N_A)^{1/3}$. Molar volumes of the studied materials $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) are not known, as far as we know. Nevertheless, molar volumes of $Ge_2Sb_2Se_5$ glass (V_M = 17.3 cm³/mol) and $Ge_2Sb_2Te_5$ (V_M = 19.6 cm³/mol – estimated from temperature dependence of V_M) were found in papers published by Gunasekera et al. [56] and Schumacher et al. [57], respectively. Then, we may expect that the values of V_M for the studied compositions would be found between those for pure $Ge_2Sb_2Se_5$ and $Ge_2Sb_2Te_5$. This assumption provides us with structural units sizes to be in the range of 3.06 – 3.19 Å. Concerning this region, the values of the a_0 parameters found for the studied samples (Table 5) provide more than ten-times (for NG model) and hundred-times (for SDG model) lower values. The exact explanation for such low and unphysical values of the a_0 parameter is unknown.

CONCLUSION

Crystal growth, viscosity and melting processes were studied in the $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) materials to provide information about the crystal growth in this system in wide temperature range.

Viscosities were measured in the range of $10^{7.5}$ - $10^{12.5}$ Pa·s. The temperature dependence was described using the simple Arrhenius type equation and the values of activation energies of viscous flow, fragilities and viscosity glass transition temperatures were determined for both compositions. The obtained fragility index is close to 43, which means, that the studied materials belong to the so-called "intermediate" liquids. Such materials, or better, their viscosity dependence on temperature cannot be extrapolated using the simple exponential dependence. Hence, more sophisticated equations are needed to be applied. Here we used the MYEGA equation to extrapolate the viscosity data into the temperature region of the studied crystal growth.

Isothermal growth of crystalline surface layer was studied using microscopy in the $Ge_2Sb_2Se_{5-x}Te_x$ (x = 0.5 and 1) undercooled melts. Analysis of the growth data revealed a crystal growth driven by the liquid-crystal interface kinetics. The growth data were scaled with viscosities to test the Stokes-Einstein-Eyring relation and no decoupling of the viscosity-growth rate relation was observed. Therefore, the crystal growth was described using standard crystal growth models. Two growth models – normal and screw dislocation, were used to describe the experimental data. Both models describe the growth data with similar accuracy. It is practically impossible to distinguish, which model should be used for description of the presented data without knowledge of the high temperature growth data.

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Figures and tables caption:

Figure 1 Crystal growth in $Ge_2Sb_2Se_{4.5}Te_{0.5}$ (a-d) and $Ge_2Sb_2Se_4Te_1$ (e-h) bulks. Typical morphology of formed crystals is shown in partially (a, e) and fully (b, f) crystallized surface of the samples. Fractures of the samples are shown at the beginning of the formation of the crystalline layer (c, g) and when the compact surface crystalline layer is formed (d, h).

Figure 2 Evolution of the formed crystalline layer thickness with annealing time for selected temperatures in undercooled $Ge_2Sb_2Se_{5-x}Te_x$ melts

Figure 3 Linearized temperature dependence (solid lines) of crystal growth rates (full symbols) in $Ge_2Sb_2Se_{5-x}Te_x$ undercooled melts together with experimental viscosities (opened symbols) measured by penetration method. The Arrhenius (dotted lines) and MYEGA (dashed lines) fits through experimental viscosity data are also depicted including the extrapolations to the temperature region where the crystal growth was measured (see the text for more information).

Figure 4 DSC measurements of amorphous (full lines) and fully crystallized (dashed lines) $Ge_2Sb_2Se_{5-x}Te_x$ samples at the heating rate of 5 °C/min.

Figure 5 Dependence of the reduced crystal growth rate (U_R) on undercooling (ΔT) in the $Ge_2Sb_2Se_{5-x}Te_x$ system. The typical error bar of the data is shown by one point for illustrative purposes.

Figure 6 Verification of decoupling between kinetic part of crystal growth rate and viscosity in the $Ge_2Sb_2Se_{5-x}Te_x$ undercooled melts

Figure 7 Crystal growth rates in the $Ge_2Sb_2Se_{5-x}Te_x$ system described by NG model (dashed lines) and SDG model (solid lines).

Table 1 Crystal growth rates in the $Ge_2Sb_2Se_{5-x}Te_x$ undercooled melts

Table 2 Viscosities of the $Ge_2Sb_2Se_{5-x}Te_x$ glasses and undercooled melts

Experimental points are marked according to indenter which was used for their determination; hemispherical indenter (•), cylindrical indenter – 1 mm in radius (^{1}) and 2 mm in radius (^{2}). Accuracy of temperature measurement is ± 0.5 °C, accuracy of viscosity measurement is ± 0.05 log units.

Table 3 Values of kinetic fragility (m), viscosity glass transition temperature (T_{12}) and activation energy of viscous flow (E_η) for $Ge_2Sb_2Se_{5-x}Te_x$ system (x = 0 was previously published by Barták et al. [37]). The apparent activation energy (Δh^*) of structural relaxation published by Svoboda et al. [30] is also listed.

Table 4 Parameters of MYEGA equation describing the viscosity dependence on temperature in the $Ge_2Sb_2Se_{5-x}Te_x$ glasses and undercooled melts.

Table 5 Parameters of the crystal growth models describing temperature dependence of crystal growth rate in the $Ge_2Sb_2Se_{5-x}Te_x$ system.

Table 1

T (°C)	x = 0.5 u (μm/min)			T (°C)	x = 1 u (μm/min)		
268.8	0.039	±	0.010	265.5	0.063	±	0.006
283.5	0.35	±	0.02	271.5	0.091	±	0.007
289.0	0.64	±	0.04	278.4	0.30	±	0.02
289.3	0.47	±	0.02	282.9	0.93	±	0.07
292.4	0.71	±	0.05	287.5	1.15	±	0.11
297.9	1.9	±	0.2	292.8	2.3	±	0.3
299.4	3.2	±	0.6	292.9	2.5	±	0.2
300.2	3.5	±	0.3	295.7	3.0	±	0.3
300.8	2.25	±	0.11	298.0	5.3	±	0.5
304.3	5.16	±	0.03	300.5	11.3	±	0.8
308.0	6.5	±	0.3	307.0	9.0	±	0.5
308.5	9.9	±	1.2	311.5	22.4	±	1.3
313.8	10.3	±	0.7	311.9	12.9	±	1.9
317.1	16.2	±	1.2	315.5	35	±	3
319.1	15.9	±	0.7	315.8	31	±	5
319.5	20.6	±	1.9	324.2	125.9	±	0.7
321.4	18.3	±	1.1				
322.5	20.5	±	1.0				
325.0	40	±	3				
326.5	38	±	4				
333.0	84	±	6				
336.5	126	±	10				

Table 2

x = 0.5		x = 1	
T (°C)	log (η/Pa·s)	T (°C)	log (η/Pa·s)
225.3	12.33•	215.5	12.34•
229.9	11.95•	217.7	12.22•
232.3	11.68•	221.7	11.83•
234.9	11.53•	223.1	11.67•
239.5	11.19[1]	230.6	11.08•
241.6	11.01[1]	235.1	10.76•
241.5	10.87•	236.0	10.66•
244.6	10.66[1]	238.6	10.51•
246.6	10.59•	243.0	10.10•
250.6	10.26•	246.9	9.87[1]
252.5	10.18[1]	249.5	9.66[1]
254.0	9.92•	255.6	9.08[1]
256.8	9.75[1]	261.9	8.65•
258.2	9.74[1]	266.2	8.27[1]
262.2	9.36[1]	270.4	7.98[1]
262.9	9.33[1]		
267.4	9.03[1]		
266.3	8.99•		
269.8	8.81[2]		
269.0	8.79[2]		
271.5	8.65[2]		
271.7	8.57[1]		
275.4	8.32[1]		
276.1	8.32[1]		
276.3	8.23[1]		
280.4	7.97[1]		
280.5	7.97•		
284.9	7.68[2]		

Table 3

	x = 0	x = 0.5	x = 1
m	43.1 ± 0.4	43.4 ± 0.3	42.8 ± 0.4
T_{12} (°C)	237 ± 2	229.3 ± 0.5	219.9 ± 0.5
E_η (kJ/mol)	421 ± 3	417 ± 3	404 ± 4
Δh^* (kJ/mol)	415 ± 6	446 ± 7	476 ± 8

Table 4

	x = 0.5	x = 1
log (η_0/Pa·s)	-5	-5
B (K)	1350 ± 43	1454 ± 71
C (K)	929 ± 17	864 ± 25

Table 5

	x = 0.5	x = 1
	a_0 (Å)	a_0 (Å)
NG model	0.199 ± 0.003	0.218 ± 0.008
SDG model	0.0331 ± 0.0006	0.0415 ± 0.0017