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**Kinetics of processes in the volume and at the surface of amorphous  
materials**

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## References

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## Abstract

Due to their outstanding properties, chalcogenide glass-forming materials have been the focus of interest among the scientific community for several decades heretofore. Developing novel technologies and applications demands a deep characterization of the behavior of these materials under certain conditions. One of the most common phenomena present in chalcogenide materials is the crystallization. Crystallization has both positive (as is the case of *Phase Changing Materials – PCM*) and negative effect (as is the case of crystallization at the surface of solar panels) on the materials quality.

In this thesis, an exhaustive study of the crystallization behavior in several chalcogenide glass-forming materials is presented. The crystal growth process was studied in various chalcogenide glass-forming materials such as pure selenium (*Se*), *Se<sub>95</sub>Te<sub>5</sub>* system and *(GeSe<sub>2</sub>)<sub>x</sub>(Sb<sub>2</sub>Se<sub>3</sub>)<sub>1-x</sub>* pseudobinary system. Crystallization process was analyzed combining several methods such as microscopy techniques (Infrared, Optical, Scanning Electron Microscopy SEM, Atomic Force Microscopy AFM), methods of thermal analysis (DSC, TMA) and methods of structural analysis (XRD).

## Abstrakt

Díky svým mimořádným vlastnostem, chalkogenidové sklotvorné materiály jsou středem pozornosti ve vědecké společnosti již několik let. Rozvoj nových technologií a aplikací vyžaduje charakterizaci těchto materiálů za určitých podmínek. Jeden z nejběžnějších dějů přítomných v chalkogenidových materiálech je krystalizace. Krystalizace má jak pozitivní (např. materiály s fázovou změnou), tak negativní (např. krystalizace na povrchu solárních panelů) dopad na kvalitu daného materiálu.

V předložené disertační práci je prezentováno podrobné studium krystalizace v několika chalkogenidových sklotvorných materiálech. Proces krystalizace byl studován v čistém selenu (*Se*), v systému *Se<sub>95</sub>Te<sub>5</sub>* a v pseudobinárním systému *(GeSe<sub>2</sub>)<sub>x</sub>(Sb<sub>2</sub>Se<sub>3</sub>)<sub>1-x</sub>*. Krystalizace byla studovaná pomocí mikroskopických metod (např. Infračervená, Optická, Skenovací Elektronová SEM a Atomová Mikroskopie), metod termické analýzy (např. DSC, TMA) a metod strukturní analýzy (XRD).

## Keywords

Chalcogenide glass, Crystal growth, Viscosity, Diffusion, Microscopy, Thermal analysis, XRD

## Klíčová slova

Chalkogenidové sklo, Růst krystalu, Viskozita, Difúze, Mikroskopie, Termická analýza, XRD

## Table of Contents

Introduction.....	5
1. Theory.....	5
1.1 Synthesis of glass.....	5
1.2 Crystallization.....	6
1.2.1 Nucleation.....	6
1.2.2 Crystal growth.....	7
2. Aims of Doctoral Dissertation.....	9
3. Results and Discussion.....	10
3.1 Se and $\text{Se}_9\text{Te}_5$ .....	10
3.2 $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ pseudobinary system.....	12
4. Conclusions.....	16
List of References.....	18
List of Published Works.....	20

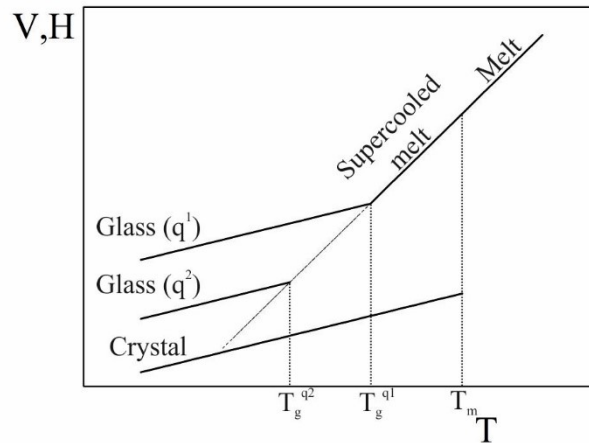
## Introduction

Since ancient times, glass has been present in the development of humankind. Apart from its decorative uses glassy materials have been a convenient ally in the development of many technologies. Chalcogenide glasses in particular have been a center of big interest among the scientific community during the last decades. Due to their exceptional properties, they are a crucial material during the development and fabrication of new technological devices. To fabricate high-quality technological devices, it is paramount to characterize the behavior of these materials under certain conditions. One of the primary phenomena that can affect the properties of glassy materials is crystallization. The crystal growth process has both positive and negative effects on the quality of such technological devices.

### 1. Theory

#### 1.1 Synthesis of glass

The synthesis of glass-forming materials is presented in Figure 1, where a temperature dependence of the volume  $V$  and enthalpy  $H$  is shown. Here it is seen that when a melt is cooled down slowly through its melting point  $T_m$ , a significant decrease in material's properties ( $V$ ,  $H$ ) is observed. This is influenced by the crystallization process, which starts at temperatures below  $T_m$ . As temperature continues decreasing, so does the volume of the crystal, however, this volume decrease is not as notable as the volume decrease of the solidifying melt. This is due to the expansion coefficient differences between both melt and crystal [1]. Since the structural particles had enough time to arrange into a periodical structure (i.e. crystalline phase), the material is in equilibrium. In order to avoid the crystallization process, it is necessary to cool down the melt rapidly (i.e. the cooling rate  $q$  is a key factor during the synthesis of glass, as is shown in Figure 1  $q^1 > q^2$ ) [2]. By cooling the melt rapidly, as is presented in Figure 1, the volume and enthalpy of the material continue decreasing unceasingly until the glass transition temperature  $T_g$  is reached. At lower temperatures the viscosity of the material rises and the mobility of structural units (atoms, molecules) becomes lower and lower. Then, the crystallization process becomes less and less feasible [1, 3, 4].



**Figure 1:** Temperature dependence of volume ( $V$ ) or enthalpy ( $H$ ) of a glass-forming material

## 1.2 Crystallization

Crystallization can be defined as the transformation from non-ordered glassy state to ordered crystalline state. This process is composed of two elemental steps: nucleation and crystal growth. During nucleation, structural precursors (nuclei) are formed. Additional incorporation of structural units to the stable nucleus results in crystal growth.

### 1.2.1 Nucleation

The nucleation process is described by the classical nucleation theory (CNT). This theory assumes that between two individual phases separated by an interphase of zero thickness, a thermodynamic equilibrium exists. CNT expresses the formation of stable clusters (i.e. the crystal growth can occur only on these clusters) with critical size  $r^*$  (i.e. supercritical cluster) [5]. Nucleation can be homogeneous or heterogeneous. The differences between both types of nucleation lie in the probability of cluster formation along the material. In the case of the homogeneous nucleation, the clusters form with the same probability (homogeneously) in every part of the sample. On the other hand, during the heterogeneous nucleation clusters are formed mostly in specific places such as dislocations or surface defects. This is because at these places the thermodynamic barrier that controls the nucleation process is smaller than the thermodynamic barrier for the homogeneous nucleation [5-7].

#### 1.2.1.1 Homogeneous nucleation

CNT describes nucleation as a casual process dependent on thermodynamics [6]. The thermodynamic barrier  $W^*$  needed to form nuclei with a spherical shape during

homogeneous nucleation corresponds to the change of the Gibbs free energy and is expressed by the following equation:

$$W^* = 4\pi r^2 \sigma_{int} - \frac{4}{3}\pi r^3 \Delta G_V \quad (1)$$

where  $r$  represents the size of the nucleus,  $\sigma_{int}$  is the interfacial free energy between the forming nucleus and the amorphous phase and  $\Delta G_V$  represents the free energy difference between the melt and crystalline phase [8, 9]. As it was mentioned previously, crystal growth process occurs only on stable nuclei with critical size  $r^*$ . At this point,  $W^*$  reaches maximal value  $W^*_{max}$ . From Eq. 1 under the assumption that the nuclei are formed as spherical particles,  $r^*$  can be calculated as follows:

$$\frac{\delta W^*}{\delta r} = 8\pi r \sigma_{int} - 4\pi r^2 \Delta G_V = 0 \quad (2)$$

$$r^* = \frac{2\sigma_{int}}{\Delta G_V} \quad (3)$$

Then by combining Eq. 1 and Eq. 3,  $W^*_{max}$  is expressed as:

$$W^*_{max} = \frac{16}{3}\pi \frac{\sigma_{int}^3}{\Delta G_V^2} \quad (4)$$

### 1.2.1.2 Heterogeneous nucleation

From the thermodynamic point of view as was mentioned previously, heterogeneous nucleation is characterized by a lower thermodynamic barrier than  $W^*$ . This is due to the decrease of surface energy, which is affected by the presence of impurities or structural defects in the material. The thermodynamic barrier for the formation of supercritical nuclei during heterogeneous nucleation ( $W^*_{Het}$ ) is expressed by:

$$W^*_{Het} = W^* \cdot \phi \quad (5)$$

where  $\phi$  is a correcting factor, which acquires values from 0 to 1. This factor is directly proportional to the contact angle ( $\theta$ ) between the supercooled liquid and a certain surface [10].

### 1.2.2 Crystal growth

Crystal growth is the main topic of study in this dissertation thesis. Crystal growth rate  $u$  is dependent on two individual factors such as thermodynamic  $F(T)$  and kinetic term  $u_{kin}(T)$ .

$$u(T) = u_{kin}(T) \cdot F(T) \quad (6)$$

$u_{kin}(T)$  is related to the mobility of structural units through the liquid-crystal interface.  $u_{kin}(T)$  is proportional to the diffusion coefficient  $D(T)$ . Since  $D(T)$  data are often missing

for chalcogenide glass-forming materials,  $D(T)$  is usually substituted with the viscosity  $\eta(T)$ . This is in concordance of the Stokes-Einstein equation ( $SE$ ), which states that the diffusion coefficient is proportional to the reciprocal value of viscosity.

$$u_{kin}(T) \propto D(T) \propto \eta(T)^{-1} \quad (7)$$

However in some cases the  $SE$  relation is found lacking and it is necessary to calculate a correcting parameter  $\xi$ , that represents the extension of decoupling between  $D(T)$  and  $\eta(T)$ [11-13].

$$u_{kin}(T) \propto \eta(T)^{-\xi} \quad (8)$$

The decoupling of  $u_{kin}$  and  $\eta$  is observed only on several types of samples. For example, the crystal growth mechanism in the volume of a sample is linked with the viscous flow of the studied material. Then  $\xi$  finds its value close to 1, which means that the kinetic part of the crystal growth rate can be substituted by  $\eta$  according to  $SE$ . On the other hand, for crystal growth in thin films and at the surface of bulk samples the mechanism is different. In our previous research on the crystal growth in chalcogenide glasses, a strong decoupling of  $SE$  is observed [14, 15]. This reveals that the crystal growth kinetics in such samples is not influenced by the viscous flow, but by the surface diffusion.

On the other hand,  $F(T)$  represents the energetic barrier that has to be overpassed to enable the crystal growth.  $F(T)$  is expressed by the following equation:

$$F(T) = 1 - \exp\left(-\frac{\Delta G}{R \cdot T}\right) \quad (9)$$

where  $\Delta G$  represents the change of the Gibbs free energy between the crystalline and amorphous phase,  $R$  is the universal gas constant and  $T$  is the temperature [16].  $\Delta G$  is a function of temperature and can be expressed as the difference of the heat capacity  $\Delta C_p$  between the crystalline and the amorphous phase [17].

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} - \int_T^{T_m} \Delta C_p(T) dT + T \int_T^{T_m} \frac{\Delta C_p(T)}{T} dT \quad (10)$$

where  $\Delta H_m$  is the enthalpy of melting. Due to the complexity of measurement of  $\Delta C_p$  among the crystallization region in the case of chalcogenide-based materials, the heat capacity data is frequently missing. For this reason, several approximations were proposed to estimate  $\Delta G$  [18-20]. However, the most appropriate and widely applied is the Turnbull approximation [21]:

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} \quad (11)$$

Since the measurement of the crystal growth and subsequent calculation of the crystal growth rate  $u(T)$  for a wide temperature range is not always possible using microscopic techniques, crystal growth models are used. These crystal growth models are: Normal growth model ( $NG$ ), Screw-dislocation growth model ( $SDG$ ) and the 2D-surface nucleated growth model [16, 22].  $NG$  assumes that the liquid-crystal interface is



atomically rough and that allows structural units to attach to any active site along with the forming crystalline phase. For this model,  $u(T)$  is expressed as:

$$u(T) = f \cdot \frac{k_B \cdot T}{3 \cdot \pi \cdot a_0^2 \cdot \eta} \cdot \left[ 1 - \exp\left(-\frac{\Delta G}{R \cdot T}\right) \right] \quad (12)$$

where  $a_0$  is the interatomic distance,  $k_B$  corresponds to the Boltzmann constant,  $R$  is the universal gas constant and  $f$  represents the number of active sites in the crystalline phase, where the structural units can attach. In this case,  $f$  is equal to 1 [12].

*SDG* model assumes that crystals grow in specific places of the sample, forming a screw-like structure [23, 24]. For this model  $u(T)$  is estimated by Eq. 12, however  $f$  is different. For this model,  $f$  is calculated by the following relation:

$$f \cong \frac{\Delta T}{2\pi \cdot T_m} \quad (13)$$

where  $\Delta T$  is the undercooling ( $\Delta T = T_m - T$ ) and  $T_m$  is the melting temperature.

2D-surface nucleated model assumes that structural units can attach at the edges of a rough crystalline layer enabling a lateral growth [25].  $u(T)$  is expressed as:

$$u(T) = \frac{C_{2D}}{\eta} \exp\left(-\frac{B}{T \Delta T}\right) \quad (14)$$

where  $C_{2D}$  and  $B$  are empirical parameters.

## 2. Aims of Doctoral Dissertation

This doctoral dissertation gives a comprehensive analysis of the crystal growth kinetics in several chalcogenide glass-forming materials. Although several studies of the crystal growth process in glass-forming materials were published already, this thesis presents a deep study of the crystal growth mechanism and crystal growth kinetics and its relation to diffusion and viscosity data.

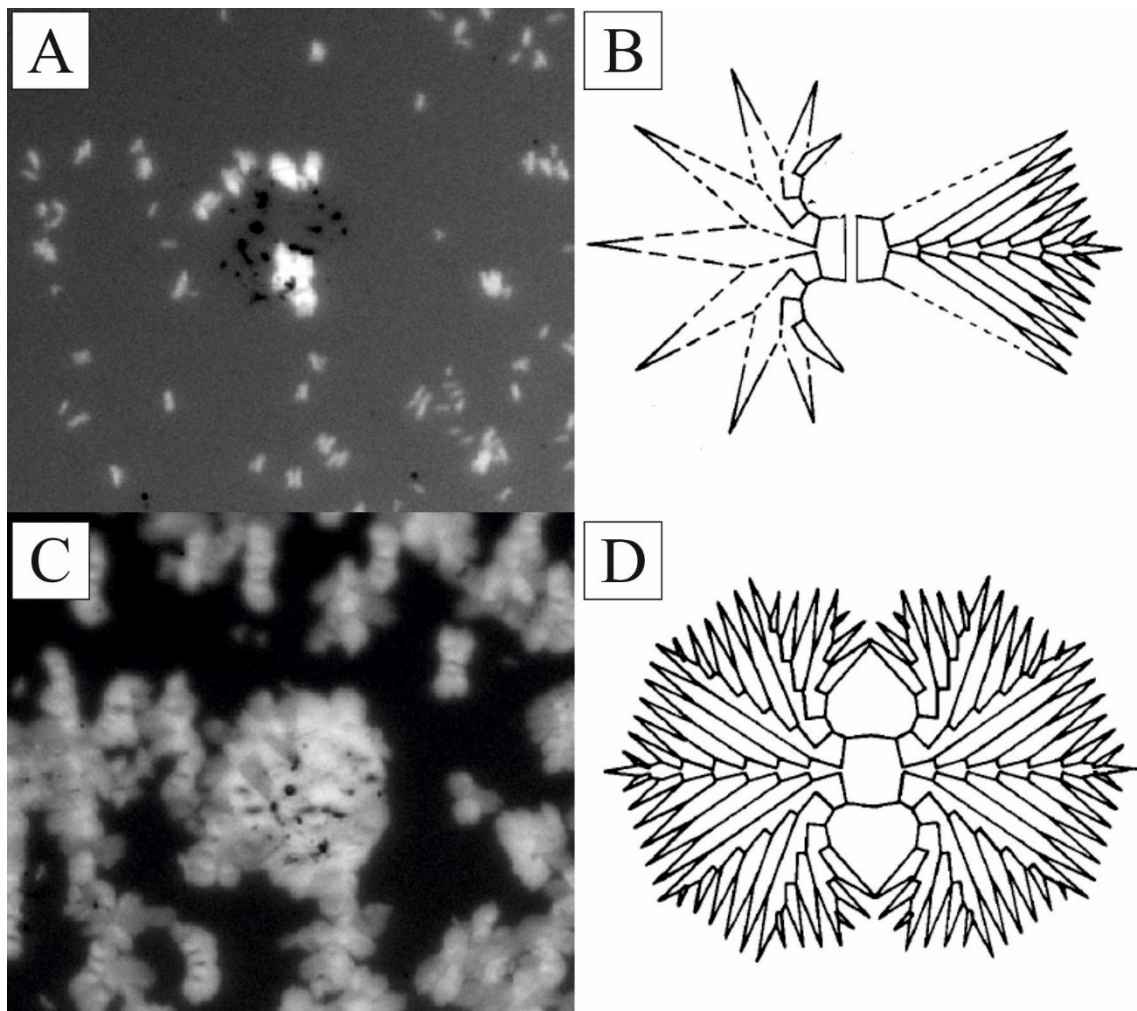
The main aims of this dissertation were divided into two parts. The first part is focused on the extensive study on crystal growth in different samples of amorphous *Se* and *Se<sub>95</sub>Te<sub>5</sub>*, which is supported with viscosity measurements in *Se<sub>95</sub>Te<sub>5</sub>* melts. Together these works bring a new insight into the competing volume and surface crystal growth with respect to the viscosity and surface diffusion in *Se* and *Se<sub>95</sub>Te<sub>5</sub>* glass formers.

The second part is dedicated to the crystal growth in *(GeSe<sub>2</sub>)<sub>x</sub>(Sb<sub>2</sub>Se<sub>3</sub>)<sub>1-x</sub>* glass-formers (from  $x = 0.4$  to  $0.9$ ). In this part, a direct study of the crystal growth kinetics in the *(GeSe<sub>2</sub>)<sub>x</sub>(Sb<sub>2</sub>Se<sub>3</sub>)<sub>1-x</sub>* system and its relation to the viscous flow and diffusion was presented. For *GeSe<sub>2</sub>-rich* compositions ( $x = 0.6 - 0.9$ ), an exhaustive *DSC* analysis was performed to obtain a deeper grasp on the complex crystal growth behavior in such samples.

### 3. Results and Discussion

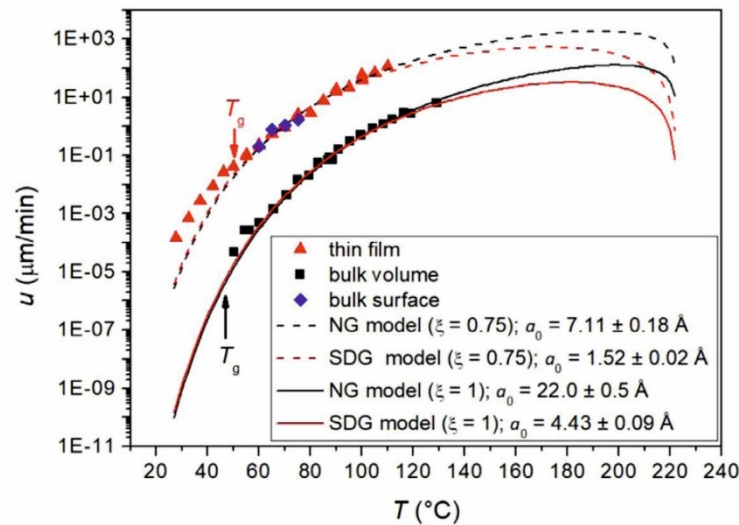
#### 3.1 Se and Se<sub>95</sub>Te<sub>5</sub>

This study presents a deep analysis of the crystal growth process in *Se* and *Se<sub>95</sub>Te<sub>5</sub>* samples. The crystal growth behavior in *Se* was compared in several types of samples such as thin films (0.2, 1 and 2  $\mu\text{m}$  of thickness) and bulk samples. Particularly, the lateral crystal growth was compared between both thin films and at the surface of bulk samples. Crystals in thin films grew as spherulitic-like structures. The crystal growth mechanism observed in thin films was comparable to crystal structures observed in previous studies [26, 27]. In the case of the crystal growth at the surface of bulk samples, the growth mechanism was more complex than the observed in thin films. At the first stage, the crystals formed sheaf-like structures, which continued branching and then spherulitic-like structures were formed. Such growth mechanism was already described by Bisault et al. [28].



**Figure 2:** Comparison between the observed crystal growth at the surface of bulk samples (A and C) and the crystal growth mechanism described by Bisault et al. (B and D)

The crystal growth rate for both thin films and at the surface of bulk samples was calculated for a wide temperature range and according to the obtained results, the crystal growth rate in thin films and at the surface of bulk samples is comparable. According to previous studies [17, 29] and the obtained results for both *Se* [14] and *Se<sub>95</sub>Te<sub>5</sub>* [30] system, the crystal growth in thin films and at the surface of bulk samples occur at faster rates than the growth in the volume of bulk samples (see Figure 3). Continuing with the analysis of the crystal growth kinetics, a crucial phenomenon was revealed. The crystal growth mechanism in thin films and at the surface of bulk samples presented a strong decoupling of *SE* ( $\xi = 0.67 \pm 0.03$ ). This is linked to the fact that structural units in thin films and at the surface of bulk samples have a different mobility than in the volume of bulk samples. Then it was possible to state that the crystal growth kinetics in thin films and at the surface of bulk samples are controlled by the surface diffusion rather than by the viscous flow, which is confirmed in the recent work of Barták et al. [31]. Similar results were obtained for crystal growth kinetics in thin films and at the surface of *Se<sub>95</sub>Te<sub>5</sub>* bulk samples ( $\xi = 0.75 \pm 0.02$ ). Also, the crystal mechanism in *Se<sub>95</sub>Te<sub>5</sub>* thin films is comparable to the mechanism observed at the surface of *Se* bulk samples. For the volume crystal growth kinetics,  $\xi = 0.97$  was calculated, which confirms that the volume mobility of structural units through the liquid-melt interface is driven by the viscous flow.



**Figure 3:** Comparison of crystal growth rates in *Se<sub>95</sub>Te<sub>5</sub>* samples [30]

For *Se<sub>95</sub>Te<sub>5</sub>* thin films, the crystal growth process was studied even below  $T_g$  as is shown in Figure 3. For temperatures below  $T_g$ , the correcting parameter  $\xi$  decreased to 0.52. This remarkable decrease of  $\xi$  value confirms a change in the crystal growth mechanism, which leads to the increase in the crystal growth rate for temperatures below  $T_g$  as is shown in Figure 3. This could be caused by a different growth mechanism comparable with the so-called Glass-Crystal (GC) mode [32].

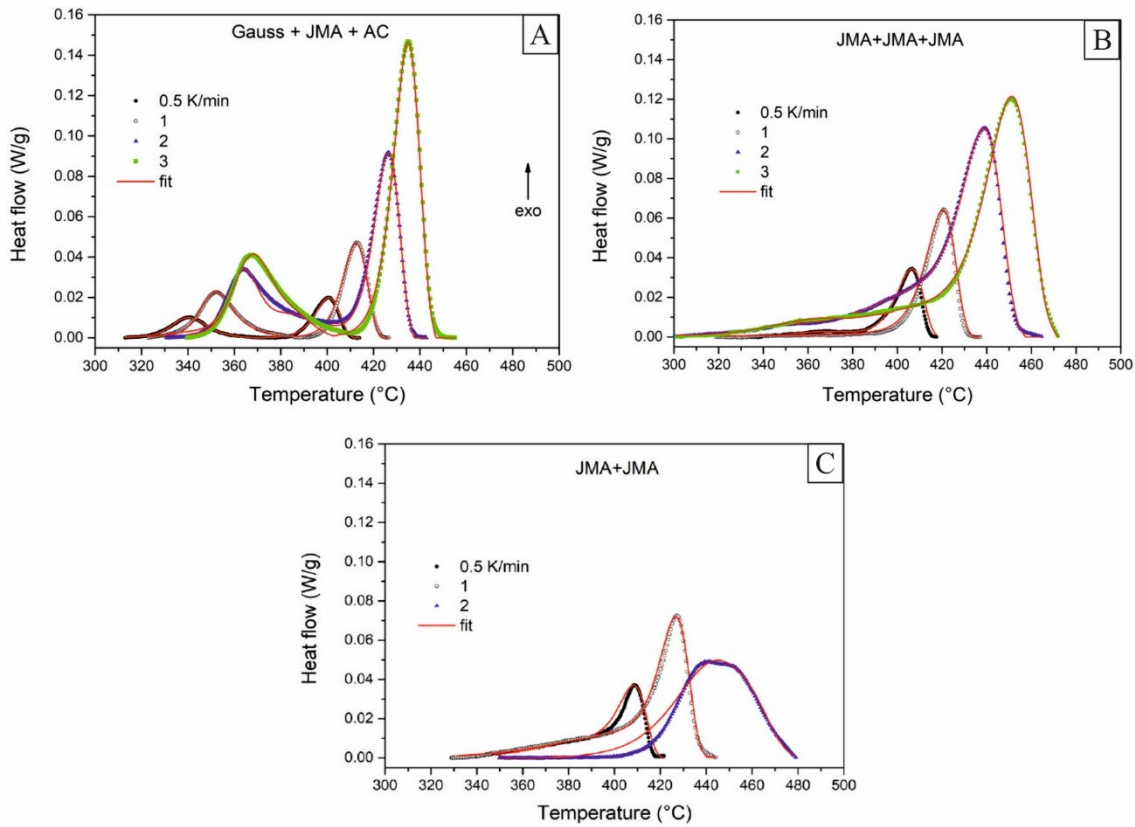
The presented study of the volume crystal growth in *Se<sub>95</sub>Te<sub>5</sub>* bulk samples revealed an interesting phenomenon. According to previous studies in *Se* and *Se-Te* glass forming materials [17, 33, 34], the spherulitic-like structures present at the surface

formed a compact crystalline layer. However, in  $Se_{95}Te_5$  samples such layer had a diffusive character (i.e. the layer was not compact). This diffusive behavior was linked to several facts. The diffusive character could have been caused by a faster nucleation process along the vicinity of the surface than in its core, or, by the intrusion of some fiber-like crystals, which grew among the crystalline layer towards the inner part of the sample. Then it is possible to state that this crystal growth mechanism was influenced by a higher mobility in the vicinity of the surface. This impeded the calculation of the crystal growth rate of this crystalline layer. For this reason, the volume crystal growth rate was estimated by measuring the diameter of the fiber-like crystals and its change in time.

### 3.2 $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ pseudobinary system

The study of the complex crystallization process in  $(GeSe_2)_x(Sb_2Se_3)_{1-x}$  glass-forming materials was performed by combining several experimental methods. The direct observation (microscopy techniques) of the crystal growth process was combined with indirect methods such as *DSC* and *XRD*. The crystal growth process was studied in bulk and powder samples.

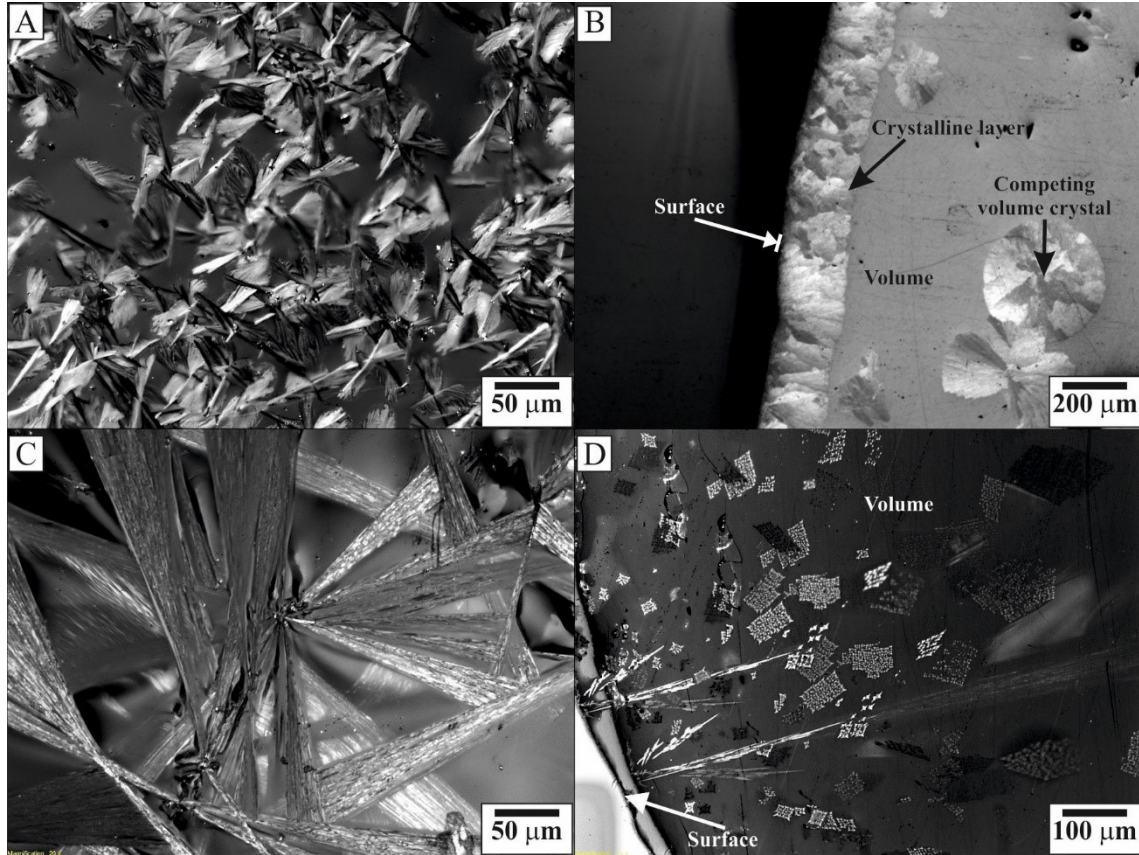
According to previous *DSC* studies [35, 36], for  $(x = 0.3 - 0.5)$  compositions, only one crystallization peak was observed under both isothermal and non-isothermal conditions. This peak corresponded to  $Sb_2Se_3$  crystalline phase. For *GeSe<sub>2</sub>-rich* compositions  $(x = 0.6 - 0.9)$ , *DSC* scans revealed a very complex crystallization process, which corresponded to the growth of both  $Sb_2Se_3$  and  $GeSe_2$  crystalline phases. Since the crystallization process which took place in the region between  $T_g$  and eutectic melting presented a very complex behavior, the *DSC* scans were performed at very slow heating rates to split up individual kinetic processes and subsequently analyze the complex crystallization process before the eutectic melting point was reached. In the case of bulk samples, the crystallization process was very slow and it was interrupted by the eutectic melting before it was completed, even at low temperatures. According to results presented in this thesis and in the study presented by Svoboda [36], crystal growth of  $Sb_2Se_3$  at the surface of bulk samples and in powder samples  $(x = 0.3 - 0.5)$  was observed at lower temperatures. This shift is related to the fact that with decreasing particle size, the surface area of the sample increases, providing a larger area for the crystal growth occurring before the eutectic melting occurs. For this reason, the study of the crystallization process in *GeSe<sub>2</sub>-rich* compositions was performed only in powder samples (with particle size of 20-50 $\mu$ m and 125-180 $\mu$ m). The kinetic analysis was performed using OriTas software [37], which uses classical kinetic equations to calculate and estimate the most suitable model that can describe the experimental data. In the case of  $(x = 0.9)$  composition, *DSC* measurements showed that crystallization process started at a temperature above  $T_g$  and presented a very complicated character, which was not complete within the analyzed temperature range (see reference [38]). For this reason, *DSC* scans of  $x = 0.9$  composition were not subjected to kinetic analysis.



**Figure 4:** DSC scans for A)  $(\text{GeSe}_2)_{0.6}(\text{Sb}_2\text{Se}_3)_{0.4}$ , B)  $(\text{GeSe}_2)_{0.7}(\text{Sb}_2\text{Se}_3)_{0.3}$  and C)  $(\text{GeSe}_2)_{0.8}(\text{Sb}_2\text{Se}_3)_{0.2}$  powder samples [38]

As is shown in Figure 4, for the  $x = 0.6$  composition (Figure 4 (A)), two crystallization peaks were observed. The first peak corresponds to  $\text{Sb}_2\text{Se}_3$  crystalline phase and the second peak corresponds to  $\text{GeSe}_2$  crystalline phase. With increasing  $x$  (i.e. increasing  $\text{GeSe}_2$  content),  $\text{Sb}_2\text{Se}_3$  crystallization peak decreases and a clear detachment from the  $\text{GeSe}_2$  crystallization peak is no longer observed. This is the case for  $x = 0.7$  and  $0.8$  (Figure 4(B) and (C) respectively) compositions. Apart from DSC measurements, this thesis presents a detailed analysis of the crystal growth kinetics in  $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$  pseudobinary system using microscopy techniques. Specifically, the crystal growth was studied at the surface and in the volume of  $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$ . This is the case for  $x = 0.4$  and  $0.5$  compositions. At the surface of bulk samples, the so-called lateral growth was observed. At the beginning of the crystal growth at the surface,  $\text{Sb}_2\text{Se}_3$  crystals grew from thin needles and continued branching, as it was observed in previous studies [39]. Due to the high density of nuclei at the surface of the samples, a compact crystalline layer was formed. This layer continued growing from the surface towards the core of the studied samples. This growth mechanism was denoted as “volume crystal growth”. Apart from this compact layer, another type of volume crystal was observed. In the core of the studied samples, some spherical-like crystals were formed. This type of crystal was denoted as “competing volume crystals”. The denominated “competing volume crystals” grew separately from the compact crystalline layer. However, it is important to mention that the radius of the so-called “competing volume crystals” and the thickness of the compact crystalline layer grew at the same rate. Then, both types of crystal growth are considered as volume crystal growth.

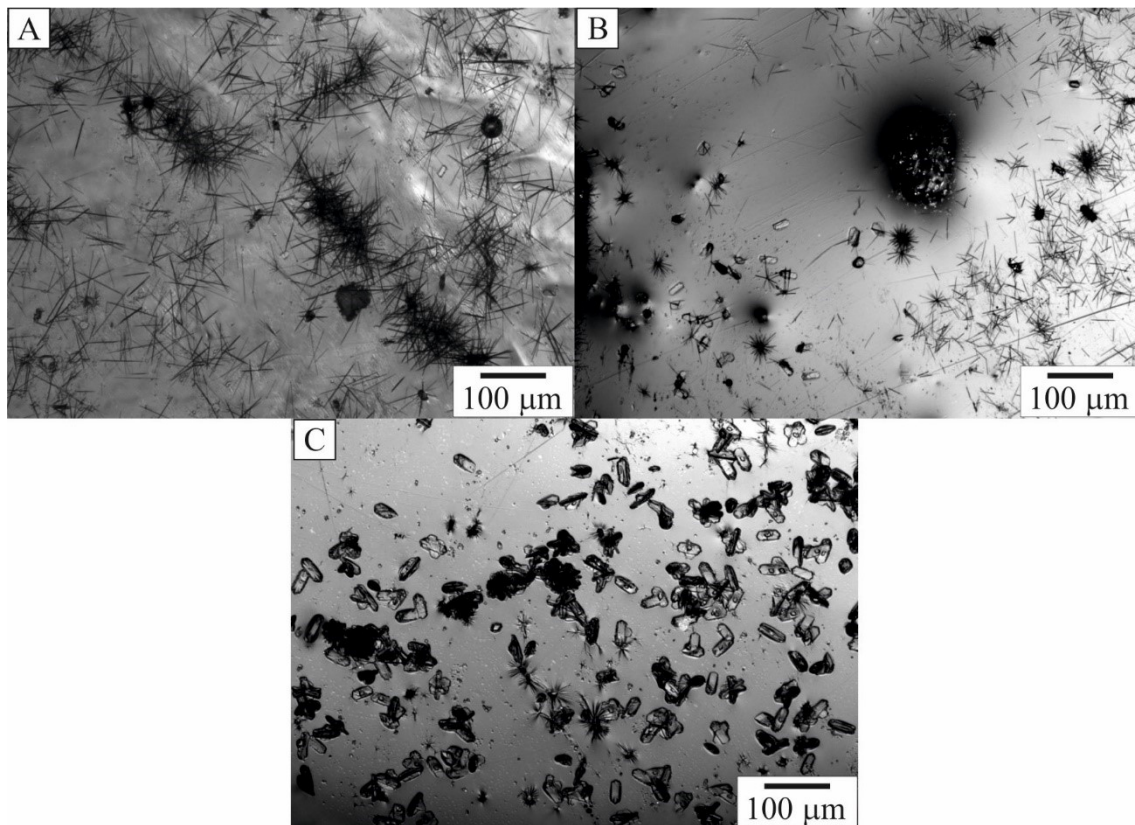
Both, surface and volume, crystal growth mechanisms were observed in both  $(GeSe_2)_{0.4}(Sb_2Se_3)_{0.6}$  and  $(GeSe_2)_{0.5}(Sb_2Se_3)_{0.5}$  compositions. In the case of  $(GeSe_2)_{0.6}(Sb_2Se_3)_{0.4}$  samples, although  $Sb_2Se_3$  crystallization process is significant according to DSC scans, no compact crystalline layer was observed (see Figure 5). For this reason, the kinetic study of the volume crystal growth was performed only in  $(GeSe_2)_{0.4}(Sb_2Se_3)_{0.6}$  and  $(GeSe_2)_{0.5}(Sb_2Se_3)_{0.5}$  compositions.



**Figure 5:** Crystal growth of  $Sb_2Se_3$  phase in  $(GeSe_2)_x(Sb_2Se_3)_{1-x}$  samples - A) Crystal growth at the surface of  $(GeSe_2)_{0.4}(Sb_2Se_3)_{0.6}$  bulk samples, B) Crystal growth towards the volume of  $(GeSe_2)_{0.4}(Sb_2Se_3)_{0.6}$  bulk samples, C) Crystal growth at the surface of  $(GeSe_2)_{0.6}(Sb_2Se_3)_{0.4}$  bulk samples, D) Crystal growth towards the volume of  $(GeSe_2)_{0.6}(Sb_2Se_3)_{0.4}$  bulk samples

A decoupling from the  $SE$  relation ( $\xi$  parameter is lower than 1) was observed in the surface crystal growth kinetics. Similar behavior was observed in previous studies [40, 41]. The decoupling parameter  $\xi$  was calculated for  $(GeSe_2)_{0.4}(Sb_2Se_3)_{0.6}$  ( $\xi = 0.7$ ),  $(GeSe_2)_{0.5}(Sb_2Se_3)_{0.5}$  ( $\xi = 0.74$ ) and  $(GeSe_2)_{0.6}(Sb_2Se_3)_{0.4}$  ( $\xi = 0.77$ ) compositions. From this data is evident that with decreasing  $Sb_2Se_3$  content,  $\xi$  finds higher values. It is then possible to state that for lower  $Sb_2Se_3$  content, the crystal growth kinetics are more influenced by the volume diffusion. On the other hand, for the volume crystal growth in  $x = 0.4$  and  $0.5$  compositions, it was concluded that the kinetic barrier and the transport of structural units from the melt to the crystal-liquid interface is driven by the volume diffusion, since for  $x = 0.4$  and  $x = 0.5$  compositions the decoupling parameter  $\xi = 0.92$  was calculated. Therefore, it is feasible to state that the volume crystal growth kinetics for both  $x = 0.4$  and  $x = 0.5$  compositions, can be described using viscosity data according to the  $SE$ .

As is shown in Figure 4 (A), for  $(GeSe_2)_{0.6}(Sb_2Se_3)_{0.4}$  samples, the crystallization process of  $Sb_2Se_3$  and  $GeSe_2$  phases occurred. Since  $Sb_2Se_3$  crystal growth started earlier (i.e. at lower temperatures) than the crystal growth of  $GeSe_2$ , at the moment when  $GeSe_2$  crystallization started, the surface was full of  $Sb_2Se_3$  crystals and it was therefore impossible to observe  $GeSe_2$  crystals using microscopy techniques. The presence of  $GeSe_2$  crystalline phase was, however confirmed by XRD analysis [38]. For  $x = 0.7$  and  $0.8$  compositions, both  $Sb_2Se_3$  and  $GeSe_2$  crystalline phases were observed as was discerned from DSC scans [38]. Apart from the DSC scans [38], both  $Sb_2Se_3$  and  $GeSe_2$  crystals were observed in  $x = 0.7$  and  $0.8$  compositions using microscopy techniques [38]. However, it is important to remark that these crystals were formed under non-isothermal conditions. From non-isothermal experiments it was impossible to estimate the crystal growth rate of both phases growing simultaneously. While studying the crystal growth kinetics in these compositions ( $x = 0.7$  and  $0.8$ ) under isothermal conditions, another crucial phenomenon was observed.



**Figure 6:**  $Sb_2Se_3$  (needles) and  $GeSe_2$  (tetragonal structures) crystals growing under isothermal conditions at  $T = 687.8$  K, A)  $t = 20$  min, B)  $t = 30$  min, C)  $t = 40$  min at the surface of  $(GeSe_2)_{0.7}(Sb_2Se_3)_{0.3}$  bulk samples.

As is shown in Figure 6, at the early stage of the isothermal treatment,  $Sb_2Se_3$  crystals are larger than  $GeSe_2$  crystals. However, during the heat treatment of the sample,  $Sb_2Se_3$  crystals became smaller while  $GeSe_2$  crystals became bigger with time (it seems that  $Sb_2Se_3$  crystals melted or dissolved after the crystal growth of  $GeSe_2$  was enhanced). For this reason, it was impossible to calculate the crystal growth rate of  $Sb_2Se_3$  at temperatures where the crystallization process of  $GeSe_2$  was predominant. In the case of

$(GeSe_2)_{0.9}(Sb_2Se_3)_{0.1}$  samples,  $Sb_2Se_3$  crystal growth was totally suppressed and only  $GeSe_2$  crystals were observed.  $GeSe_2$  growth kinetics also presented a decoupling from the  $SE$  relation, where  $\xi$  decreased with increasing  $GeSe_2$  content. However, for  $GeSe_2$  phase, the decrease of  $\xi$  is more abrupt than for  $Sb_2Se_3$ .

#### 4. Conclusions

Presented results in this thesis give a deeper grasp on the crystal growth behavior of  $Se$ ,  $Se_{95}Te_5$  and  $(GeSe_2)_x(Sb_2Se_3)_{1-x}$  chalcogenide glass-forming materials. The crystal growth kinetics were studied according to the contemporary theories about crystal growth. Main outcomes will be presented as follows.

##### **Crystal growth kinetics in $Se$ samples:**

- The crystal growth in thin films, at the surface of bulk samples and in the volume of bulk samples was compared.
- The so-called lateral surface growth was observed in thin films and at the surface of bulk samples.
- The crystal growth in thin films and at the surface of bulk samples is faster than the volume crystal growth. The crystal growth behavior for a wide temperature range in such samples was estimated by contemporary growth models ( $NG$  and  $SDG$ )
- Crystal growth kinetics in thin films and at the surface of bulk samples presented a strong decoupling of the  $SE$  relation. It was demonstrated that this might be linked to the fact that the crystal growth kinetics in such samples is driven by surface diffusion.

##### **Crystal growth kinetics in $Se_{95}Te_5$ samples:**

- The crystal growth kinetics in thin films, at the surface and towards the volume of bulk samples, and its relation to the mobility of structural units from the amorphous to the crystalline phase, was analyzed.
- Crystal growth in thin films and at the surface of bulk samples was faster than the crystal growth towards the volume of the sample.
- The crystal growth in thin films was observed even at temperatures below  $T_g$ , showing that the crystal growth mechanism changed at  $T_g$ . Due to the significant decoupling of the  $SE$  relation, for temperatures lower than  $T_g$ , parameter  $\xi$  decreased.
- The volume crystal growth in bulk samples, revealed formation of fiber-like crystalline structures which differ from the crystals observed in other  $Se-Te$  compositions.



### **Crystal growth kinetics in $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ pseudobinary system:**

- The crystal growth mechanism was studied at the surface and in the volume of bulk samples. Several compositions were analyzed (i.e. from  $x = 0.4$  to  $x = 0.9$ )
- In the case of  $x = 0.4$  and  $x = 0.5$  compositions, the crystal growth was studied at the surface and towards the volume of bulk samples. Two types of crystal growth mechanisms were observed.
- *DSC* scans revealed a very complex crystallization process. Analysis of such complex crystal growth behavior was complemented with direct microscopy study. In the case of *GeSe<sub>2</sub>-rich* compositions ( $x = 0.6 - 0.9$ ), both *Sb<sub>2</sub>Se<sub>3</sub>* and *GeSe<sub>2</sub>* crystalline phases were observed.
- The surface crystal growth kinetics of both *Sb<sub>2</sub>Se<sub>3</sub>* and *GeSe<sub>2</sub>* phases in all the compositions, presented a strong decoupling from the *SE* relation.

Dissertation thesis is focused on the study of the crystal growth behavior of several chalcogenide glass-forming materials. This thesis presents a comparison between surface and volume crystal growth mechanisms. Since crystal growth kinetics are related to viscous flow and diffusion through the liquid-melt interface, this thesis presented a deep analysis of such processes.

It is important to remark that crystallization has both positive and negative effects on some technologies and technological applications. In some cases, the crystallization process is necessary. This is the case for *Phase Changing Materials – PCM*. On the other hand, the crystallization process should be avoided because it reduces the effectivity of technological applications as is the case of optical fibers and solar panels.

For this reason, this thesis gives very valuable information about the crystal growth behavior in chalcogenide glass-forming glasses, which might be used to improve the quality of established technologies and to develop new technological devices.

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## List of Published Works

### Paper I

BARTÁK, Jaroslav, VALDÉS, Diego, MÁLEK, Jiří, PODZEMNÁ, Veronika, SLANG, Stanislav, PÁLKA, Karel. Comparison of Lateral Crystal Growth in Selenium Thin Films and Surface of Bulk Samples. *Crystal Growth and Design*, 2018, 18, 4103–4110.

### Paper II

MARTINKOVÁ, Simona, VALDÉS, Diego, SLANG, Stanislav, PÁLKA, Karel, BARTÁK, Jaroslav. Relationship between Crystal Growth and Surface/Volume Mobilities in Se<sub>95</sub>Te<sub>5</sub> Bulk Samples and Thin Films. *Acta Materialia*, 2021, 213, 116953

### Paper III

BARTÁK, Jaroslav, KOŠTÁL, Petr, VALDÉS, Diego, MÁLEK, Jiří, WIEDUWILT, Torsten, KOBELKE, Jens, SCHMIDT, Markus A.. Analysis of Viscosity Data in As<sub>2</sub>Se<sub>3</sub>, Se and Se<sub>95</sub>Te<sub>5</sub> Chalcogenide Melts Using the Pressure Assisted Melt Filling Technique. *Journal of Non-Crystalline Solids*, 2019, 511, 100-108

### Paper IV

VALDÉS, Diego, MARTINKOVÁ, Simona, MÁLEK, Jiří, BARTÁK, Jaroslav. Crystal Growth in Ge-Sb-Se Glass and its Relation to Viscosity and Surface Diffusion. *Journal of Non-Crystalline Solids*, 2021, 566, 120865

### Paper V

HONCOVÁ, Pavla, VALDÉS, Diego, BARTÁK, Jaroslav, MÁLEK, Jiří, PILNÝ, Petr, SLANG, Stanislav. Combination of Indirect and Direct Approaches to the Description of Complex Crystallization Behavior in GeSe<sub>2</sub>-rich Region of Pseudobinary GeSe<sub>2</sub>-Sb<sub>2</sub>Se<sub>3</sub> system. *Journal of Non-Crystalline Solids*, 2021, 568, 120968