

UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY

Department of Physical Chemistry

Simona Martinková

**Nucleation and Crystal Growth
in Chalcogenide Amorphous Materials**

Theses of the Doctoral Dissertation

Pardubice 2018

Study program: **Physical Chemistry**

Study field: **Physical Chemistry**

Author: **Simona Martinková**

Supervisor: **prof. Ing. Jiří Málek, DrSc.**

Year of the defense: 2018

References

MARTINKOVÁ, Simona. *Nucleation and Crystal Growth in Chalcogenide Amorphous Materials*. Pardubice, 2018. 103 pages. Dissertation thesis (PhD.). University of Pardubice, Faculty of Chemical Technology, Department of Physical Chemistry. Supervisor prof. Ing. Jiří Málek, DrSc.

Abstract

The presented doctoral thesis deals with the study of nucleation and crystal growth in chalcogenide glasses. Although a lot of papers have been published about nucleation and crystal growth during past decades and many theories have been suggested, there is still a need for more information about these complicated processes in chalcogenide glasses, in particular with respect to their indispensable technological applications. The thesis extends the understanding of crystal nucleation and growth behavior in chalcogenide glasses.

The first part of the thesis is focused on the study of nucleation kinetics in chalcogenide glass and testing of the applicability of so far proposed theories (like CNT) and their improvements for description of steady-state and transient nucleation. The second part of thesis deals with the extension of studies on crystal growth kinetics in chalcogenide glasses using direct (optical and electron microscopy) and indirect (X-ray diffraction, differential scanning calorimetry, thermomechanical analysis) methods. The combination of more approaches gave better insight into the crystal growth process. The results were described on the basis of standard and corrected growth models.

Abstrakt

Předložená disertační práce se zabývá studiem nukleace a růstu krystalů v chalkogenidových sklech. Ačkoli již bylo během uplynulých desetiletí publikováno mnoho prací zabývajících se nukleací a růstem krystalů a mnoho teorií bylo navrženo, nadále přetrvává potřeba získání více informací o těchto komplikovaných procesech a to s ohledem na nepostradatelné technologické aplikace chalkogenidových skel. Tato disertační práce obsahuje další poznatky o nukleaci a růstu krystalů v chalkogenidových sklech.

První část disertační práce je zaměřena na studium kinetiky nukleace v chalkogenidovém skle a ověření platnosti doposud navržených teorií (jako je CNT) a jejich zlepšení pro popis ustálené a neustálené nukleace. Druhá část disertační práce se zabývá studiem kinetiky růstu krystalů v chalkogenidových sklech pomocí přímých (optická a elektronová mikroskopie) a nepřímých (rentgenová difrakce, diferenciální skenovací kalorimetrie, termická analýza) metod. Kombinací více přístupů je možné získat lepší náhled na proces růstu krystalů. Výsledky byly popsány na základě standardních a korigovaných kinetických růstových modelů.

Keywords

nucleation, crystal growth, chalcogenide glass, microscopy, CNT, crystal growth models

Klíčová slova

nukleace, růst krystalů, chalkogenidové sklo, mikroskopie, CNT, růstové modely

Table of Contents

Introduction.....	5
1. Theory.....	5
1.1 Formation of Glass.....	5
1.2 Crystallization.....	6
1.2.1 Nucleation.....	7
Non-Steady-State (Transient) Nucleation.....	8
1.2.2 Crystal Growth.....	9
1.2.3 Decoupling of Viscosity and Crystallization Processes.....	10
2. Aims of Doctoral Dissertation.....	11
3. Results and Discussion.....	11
3.1 Nucleation.....	11
3.2 Crystal Growth.....	14
4. Conclusions.....	21
List of references.....	23
List of Published Works.....	25

Introduction

Glasses are important materials for modern technology, however, they have been known for centuries. Most people associate the word “glass” with traditional oxide glasses but there are also some relatively novel inorganic and organic glasses, such as chalcogenide ones. Chalcogenide glasses are non-oxide materials which contain one or more of the chalcogen elements: S, Se, or Te. Researchers are interested in glassy alloys of chalcogen elements due to their unique structural, electronic, optical and thermal properties (infrared transparency, photosensitivity, high refractive index), and hence technologically attractive applications (glass-ceramics, phase-change memories, optical and optoelectronic components used in thermal imaging systems and optical waveguides devices)¹. Some applications call for the perfect and stable glass and it is essential to avoid the crystallization process. On the other hand, the controlled and very fast amorphous to crystalline phase transformation is required for other applications.

Although many studies on structural ordering, thermal properties and nucleation and crystal growth in chalcogenide glasses have been performed, there is still a need for more detailed information.

1. Theory

1.1 Formation of Glass

Glass can be theoretically prepared from any kind of material provided sufficiently high cooling rate of liquid. In order to avoid the crystallization, the cooling rate must be high enough to ensure negligible nucleation or crystal growth. The temperature dependence of liquid's volume which can crystallize and form a glass is depicted in Figure 1. Crystallization can occur if the liquid is cooled below the temperature of melting T_m with low cooling rate. In such case, the slow cooling results in the molecules being rearranged into the regular crystalline structure. Crystallization is the first-order phase transition which usually results in a decrease in volume. In the case when the cooling rate is high enough so that the nucleation and crystal growth are avoided, the uncrystallized liquid-like material below T_m is called supercooled liquid. Further cooling of supercooled liquid is accompanied by slowing-down of viscous flow and thus inhibiting the molecular motions. At certain temperature the molecules move so slowly that they cannot rearrange into adequate configurations in the available time allowed by the cooling rate. The resulting structure of material which appears “frozen” in comparison with the laboratory timescale is denoted as glass. This transformation is manifested in the temperature dependence of volume's liquid as a continuous slow-down of the dV/dT dependence, which occurs in a narrow range of temperatures. Temperature corresponding to the intersection of extrapolated temperature dependences of volume in glassy and supercooled liquid states is called the glass transition temperature T_g . As can be seen in Figure 1, the glass transition temperature changes with cooling rate. The faster the liquid is cooled, the shorter time for molecular rearrangement is available, and hence the falling out of liquid-state equilibrium occurs at higher temperatures. Although the glass transition temperature is different for different cooling rates, the dependence of T_g on cooling rate is weak (the change in cooling rate by an

order of magnitude results in the change of T_g by 3 – 5 °C) and therefore T_g is an important material characteristic².

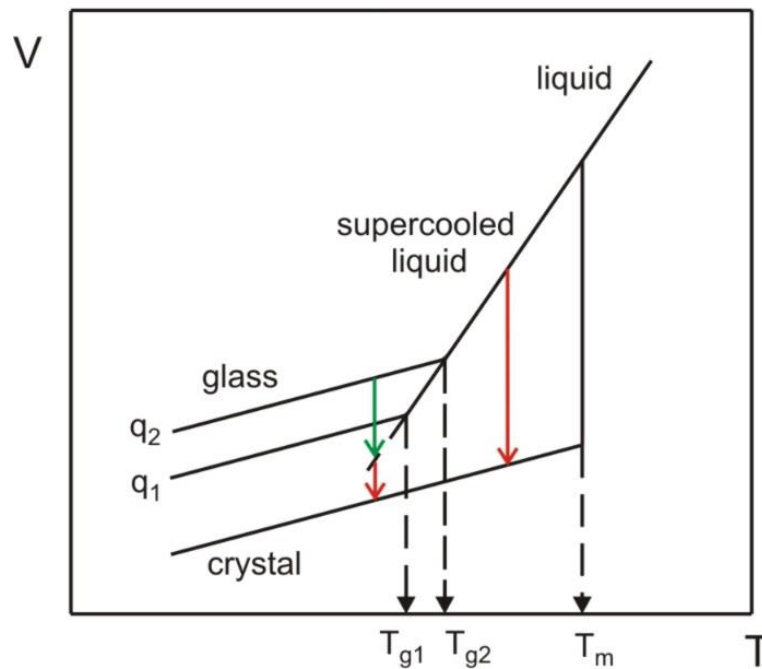


Figure 1: The dependence of liquid's volume on temperature. A slower cooling rate q_1 leads to a glass transition at T_{g1} , a faster cooling rate q_2 results in a glass transition at T_{g2} .

From the thermodynamic point of view³, glass is an unstable state which over longer times spontaneously relaxes towards equilibrium. It is usually assumed that such equilibrium corresponds to the extrapolated supercooled liquid state (indicated by the green arrow in Figure 1). Finally, upon heating or at infinitely long times at any nonzero temperature, most glasses pass into the thermodynamically stable crystal state for $T < T_m$ (red arrow in Figure 1). The supercooled liquid is a metastable state, nevertheless if no nuclei are present, it can be considered an equilibrium state. A thermodynamic barrier exists, that is necessary to be overcome so that the nucleation event can occur. The supercooled liquids also tend to crystallize after certain time at any positive temperature (red arrows in Figure 1).

1.2 Crystallization

Crystallization is a process which results in the rearrangement of liquid or amorphous structure into the regular crystalline structure. The crystallization process involves two steps:

- Nucleation
- Crystal Growth.

At first the nucleation barrier must be overcome, hence the stable nuclei of critical size are formed and are capable of a further growth.

1.2.1 Nucleation

The first step of crystallization, the nucleation process, involves the formation of precursors of the crystalline phase which is connected with the overcoming of a potential barrier by thermal fluctuations. The process of nucleation may occur by different mechanisms which are commonly divided into⁴:

- Homogeneous – nuclei are formed stochastically with the same probability in volume (surface) of sample. The number of nuclei in non-crystalline sample volume increases with time.
- Heterogeneous – nucleation occurs at preferred places such as preexisting nuclei, impurities, defects. The number of nuclei is constant with time.

Depending on the position where nucleation takes place, one can distinguish volume and surface crystallization.

According to the classical nucleation theory (CNT), which is frequently used for the analysis of crystal nucleation in glass-forming liquids, the steady-state homogeneous nucleation rate I_{st} at temperature T can be written as^{4,5}:

$$I_{st} = \frac{n_V k_B T}{h} \exp\left(-\frac{W^* + \Delta G_D}{k_B T}\right) \quad (1)$$

where W^* is the thermodynamic barrier for nucleation (i.e. increase in the free energy of a system due to the formation of a critical nucleus with size r^*), ΔG_D is the kinetic barrier for nucleation (i.e. activation free energy for move of structural units from liquid to nucleus), k_B is the Boltzmann constant, $n_V \sim 1/\lambda^3$ is the number of structural units, with a size λ , per unit volume and h is the Planck constant. The size of critical nucleus r^* and hence the thermodynamic barrier for nucleation W^* can be estimated from the following condition^{4,5}:

$$\frac{\partial W}{\partial r} = 0, \quad W = c_1 r^2 \sigma - c_2 r^3 \Delta G_V \quad (2)$$

where W is the work of nucleus formation, c_1 and c_2 are the shape factors of evolving nucleus, σ is the crystal-liquid surface energy, r is the radius of nucleus and $\Delta G_V = \Delta G/V_m$ with ΔG being the thermodynamic driving force for crystallization (i.e. the free energy difference between crystalline phase and supercooled liquid) and V_m being the molar volume. Then for a spherical nucleus, the critical nucleus size r^* and the thermodynamic barrier for nucleation W^* are given by^{4,5}:

$$r^* = \frac{2\sigma V_m}{\Delta G} \quad (3)$$

$$W^* = \frac{16\pi\sigma^3 V_m^2}{3\Delta G^2} \quad (4)$$

With the knowledge of heat capacities of crystalline phase and supercooled liquid, the thermodynamic driving force for crystallization ΔG can be calculated via equation:

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} + \int_T^{T_m} \Delta C_p dT - T \int_T^{T_m} \Delta C_p \frac{dT}{T} \quad (5)$$

where ΔH_m is the melting enthalpy, ΔT is undercooling ($\Delta T = T_m - T$) and ΔC_p is the heat capacity difference between crystalline phase and supercooled liquid at constant pressure ($\Delta C_p = C_p^{cr} - C_p^m$). Due to the often found absence of experimental data on heat capacities, several approximations of ΔG were proposed⁶⁻⁹. One of the most used expressions is assigned to Turnbull⁶ who assumed $\Delta C_p = 0$:

$$\Delta G = \Delta H_m \frac{\Delta T}{T_m} = \Delta S_m \Delta T \quad (6)$$

where ΔS_m is the entropy of melting of the crystalline phase. Regarding the kinetic barrier for nucleation, ΔG_D is usually related to the readily available experimentally obtained transport parameter, viscosity η ¹⁰. It is assumed that the molecular transport for crystallization process is controlled by diffusion and can be described in terms of an effective diffusion coefficient D . The measurement of diffusion is complicated, and the temperature dependence of diffusion coefficient is mostly not available, so D is usually expressed via the Stokes-Einstein or Eyring equation¹¹:

$$D = \frac{k_B T}{3\pi\lambda\eta} \quad (7)$$

$$D = \frac{k_B T}{\lambda\eta} \quad (8)$$

where λ is the diameter of the diffusing molecules (structural units) or jump distance.

Regarding the heterogeneous nucleation^{4,5}, the presence of preexisting nuclei, phase boundaries, dislocations, foreign solid particles may favor the nucleation process. The thermodynamic barrier for heterogeneous nucleation is lower relative to that of homogeneous nucleation owing to a decrease of the surface energy contributions to the work of critical nucleus formation ($W_{het}^* = W^* \phi$ considering the convenient spherical-cap model; ϕ is the parameter depending on the value of wetting angle). The order of favorable sites with respect to the decreasing thermodynamic barrier is: nucleation on a boundary, on an edge and at a corner⁴. Using the similar assumptions that were employed in the derivation of the steady-state homogeneous nucleation rate, it is possible to express the equation for steady-state heterogeneous nucleation rate. The number of structural units per unit volume n_V , which can be found in eq 1, is replaced by the number of structural units in contact with the catalyzing surface n_S . Then, the steady-state heterogeneous nucleation rate is given by:

$$I_{st}^{het} \cong n_S \frac{k_B T}{h} \exp \left[-\frac{W^* \phi + \Delta G_D}{k_B T} \right] \quad (9)$$

Non-Steady-State (Transient) Nucleation

Eq. 1 represents the classical model used to calculate a steady-state nucleation rate I_{st} which is independent of time. However, a lot of experiments in condensed systems indicate that the nucleation rates differ from the steady-state values in early stages of nucleation⁴. Some transient period is needed to build up the initial nuclei distribution

toward the time independent distribution corresponding to the nucleation temperature T . Cooling rates used for glass formation via melt-quench process and the rates of heating a glass up to a temperature of interest are usually too high to keep a steady-state distribution of nuclei. The time required to establish a steady-state nucleation rate is denoted as the time-lag in nucleation τ . The way for finding the characteristic quantities of transient nucleation (I_{st} , t_{ind} and τ) is by fitting the whole curve of time dependence of nuclei number ($N-t$ curve) using the appropriate model for transient nucleation.

The first expression for transient nucleation proposed by Zeldovich¹² allows one to describe the time dependent nucleation rate and find the time-lag in nucleation. The Zeldovich equation fails mainly at large times of the time dependence of nuclei number¹³, so many alternative analytical and numerical solutions¹⁴ developed from the fundamental Frenkel-Zeldovich equation⁴ were proposed for treatment of transient nucleation. One of the most famous solutions for transient nucleation was proposed by Collins and Kashchiev^{15,16}. The Collins-Kashchiev (C-K) equation is commonly used for the treatment of experimental $N-t$ data to obtain the steady-state nucleation rate and time-lag in silicate glasses. Moreover, the C-K equation provides the values of I_{st} and τ , which are in a good agreement with those from numerical solutions¹⁷. Another successful analytical solution was suggested by Shneidman¹⁸ for the time dependent nucleation rate for nuclei of sizes sufficiently larger than the critical size.

1.2.2 Crystal Growth

The second part of the crystallization process is the crystal growth. The crystal growth rate is affected by two quantities¹⁹:

- the probability of irreversible molecular attachment to the crystal (expressed in terms of the change of Gibbs free energy between the supercooled liquid and crystalline phase)
- the rate at which atoms/molecules can move from the liquid to the growing surface of crystal and can incorporate into the newly formed crystalline phase (u_{kin}).

The crystal growth rate can be controlled by three main processes²⁰: diffusion in the liquid, flow of latent heat from the surface of the growing crystal and reaction at the crystal-liquid interface. In the case of the crystal growth controlled by the kinetics at the crystal-liquid interface, the crystal growth rate is time independent and the crystal size evolves linearly with time. This type of rate controlling process is the most common for crystal growth in glasses. The crystal growth rate can be expressed by the following equation²⁰:

$$u = f \frac{D}{\lambda} \left[1 - \exp\left(-\frac{\Delta G}{RT}\right) \right] \quad (10)$$

where f is the fraction of preferred growth sites at the interface which differs according to the crystal growth model, R is the gas constant.

Three standard phenomenological models are applicable for the description of the crystal growth which is controlled by the crystal-liquid interface kinetics^{11,20}: normal growth model, screw dislocation growth model, 2D surface nucleated growth model.

The difference between the standard growth models is based on the nature of the crystal-liquid interface, i.e. the amount and type of available interfacial sites where atoms/molecules can attach to the surface of growing crystal. A simple way for the estimation of the operative crystal growth model based on the dependence of reduced crystal growth rate U_R on supercooling ΔT was proposed by Jackson²¹. The reduced crystal growth rate can be expressed by equation:

$$U_R = \frac{u\eta}{1 - \exp\left(-\frac{\Delta G}{RT}\right)} \quad (11)$$

The dependence of U_R on ΔT results in a shape of horizontal line for the normal growth model, straight line with a positive slope for the screw dislocation growth model, or a curve with increasing positive slope for the 2D surface nucleated model.

1.2.3 Decoupling of Viscosity and Crystallization Processes

The classical nucleation theory and standard growth models are based on the assumption that the molecular transport in nucleation and growth processes expressed by the diffusion coefficient can be described by temperature dependence of viscosity according to the Stokes-Einstein or Eyring relation (SE/E) ($D \approx \eta^{-1}$). This assumption was tested by several authors^{19,22-28}. Ediger et al.²³ reported u_{kin} scaling with viscosity $\sim \eta^{-\xi}$ for a wide range of organic and inorganic materials with the exponent ξ smaller than unity. They proposed a simple way to test the decoupling which is based on a power law dependence of u_{kin} on the viscosity:

$$u_{kin} \propto \eta^{-\xi} \quad (12)$$

where u_{kin} is the kinetic part of crystal growth rate ($u_{kin} = u/[1 - \exp(-\Delta G/RT)]$; defined using normal growth model) and the kinetic exponent $0 \leq \xi \leq 1$ expresses the extent of decoupling of crystal growth rate and viscosity. The slope of the dependence of $\log u_{kin}$ vs $\log \eta$ corresponds to the kinetic exponent ξ . The information about decoupling can also give a comparison of the effective diffusion coefficients calculated from the crystal growth data (Eq. 3) and from viscosity (using the SE/E equation)^{24,25}.

It was found that for strong glasses the SE/E equation describing the transport controlling crystal growth works well from T_m down to T_g , on the other hand the signs of a SE/E equation breakdown in fragile glasses were observed below approximately $1.2 T_g$. In the case of decoupling between the crystal growth and viscosity, the correction of growth models with the use of the kinetic exponent ξ ($D \approx \eta^{-\xi}$) is necessary²⁹⁻³¹ in order to achieve a good agreement between the experimental growth rate data and growth model.

Regarding the nucleation, Nascimento et al.²⁶ investigated the effects of decoupling of dynamics of crystal nucleation and growth from those of viscous flow in lithium disilicate glass. They found that the decoupling between nucleation rate and viscous flow occurs at lower temperature near T_g and that it is not so significant as that between the growth rate and viscous flow.

The possible explanation of the breakdown in scaling between the crystallization processes and viscosity is a manifestation of spatially dynamic heterogeneity in glass-forming liquids^{23,26,32} which is connected with molecular motion.

2. Aims of Doctoral Dissertation

The doctoral dissertation is focused on the study of nucleation and crystal growth in various chalcogenide glassy systems with respect to the kinetics. In order to obtain more details about crystallization, the direct microscopy observation was mainly used. The microscopy results were supplemented with those from indirect measurements (differential scanning calorimetry, X-ray diffraction, thermomechanical analysis). Although many studies have been reported about crystallization in chalcogenide glasses during past decades, there is still a need for more detailed information about mechanism and kinetics of this process due to the unsolved problems and questions.

One of the aims of the doctoral dissertation was the study of nucleation in chalcogenide glasses and testing the applicability of so far proposed theories (like CNT) and their improvements for the description of steady-state nucleation and analysis of transient models for nucleation. The crystal nucleation in glasses is studied for several decades, and many papers have been published that extend the understanding of the nucleation process and its description via classical nucleation theory (CNT). Some problems occurring in the quantitative description of nucleation rates were resolved in those papers. Nevertheless, it should be noted that the essential portion of the present knowledge on nucleation in glass forming systems is based on studies in oxide glasses. As far as we know, only a few studies of nucleation have been performed in chalcogenide glasses, which were mostly qualitative without detailed information about nucleation kinetics and quantitative data on nucleation rates.

The second goal of the presented doctoral thesis was a study of crystal growth in selected chalcogenide materials, aiming to obtain further information about crystal morphologies, crystal growth behavior and kinetics of these materials. The objective of the studies was the description of crystal growth in a wide temperature range combining experimental data obtained mainly using different direct (OM, SEM) experimental techniques with those from indirect (XRD, DSC, TMA) experimental techniques.

The studies were published in high-quality international journals in the form of 5 papers^{29,31,33-35}.

3. Results and Discussion

3.1 Nucleation

As regards the nucleation, it was difficult to find chalcogenide glassy system where number of nuclei N changes with annealing time and temperature in order to test CNT, its improvements and analysis of transient models for nucleation. According to my observations, nucleation in chalcogenide glasses occurs mostly at sample surface via heterogeneous mechanism so it is difficult to obtain any quantitative result in the form of nucleation rates. The combination of volume and surface nucleation was observed in

$\text{Se}_x\text{Te}_{1-x}$ ($x=0.1; 0.2; 0.3$) bulk glass³⁶, volume nucleation was observed in $(\text{GeS}_2)_{0.9}(\text{Sb}_2\text{S}_3)_{0.1}$ bulk glass, where it seems that nucleation occurs at fixed athermal nuclei which were formed during the preparation of glass by melt-quench technique. In comparison with silicate glasses, the induction period and time-lag for nucleation are much more shorter and nucleation is faster, hence, maybe this is the reason why it is not possible to measure nucleation rates using DSC/DTA technique. Nevertheless, some compositions of Ge-Sb-S system appear to be suitable for the quantitative study of nucleation. The Ge-Sb-S system was previously investigated by researchers from the thermodynamic and viscosity point of view^{37,38}. These data are necessary for calculations of nucleation kinetics. The study of nucleation kinetics was made in $(\text{GeS}_2)_{0.9}(\text{Sb}_2\text{S}_3)_{0.1}$ thin films using double-stage heat treatment method and optical microscopy³⁹. In the doctoral dissertation the opposite composition within the $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ row was studied (schematically depicted in Figure 2)³⁴. The crystal nucleation in $\text{Ge}_{1.8}\text{Sb}_{36.8}\text{S}_{61.4}$ thin films of $1\ \mu\text{m}$ thickness, which is close to $(\text{GeS}_2)_{0.1}(\text{Sb}_2\text{S}_3)_{0.9}$ ($= \text{Ge}_{2.1}\text{Sb}_{37.5}\text{S}_{60.4}$), was observed in-situ using optical microscope coupled with a computer-controlled heating stage in the transmission mode.

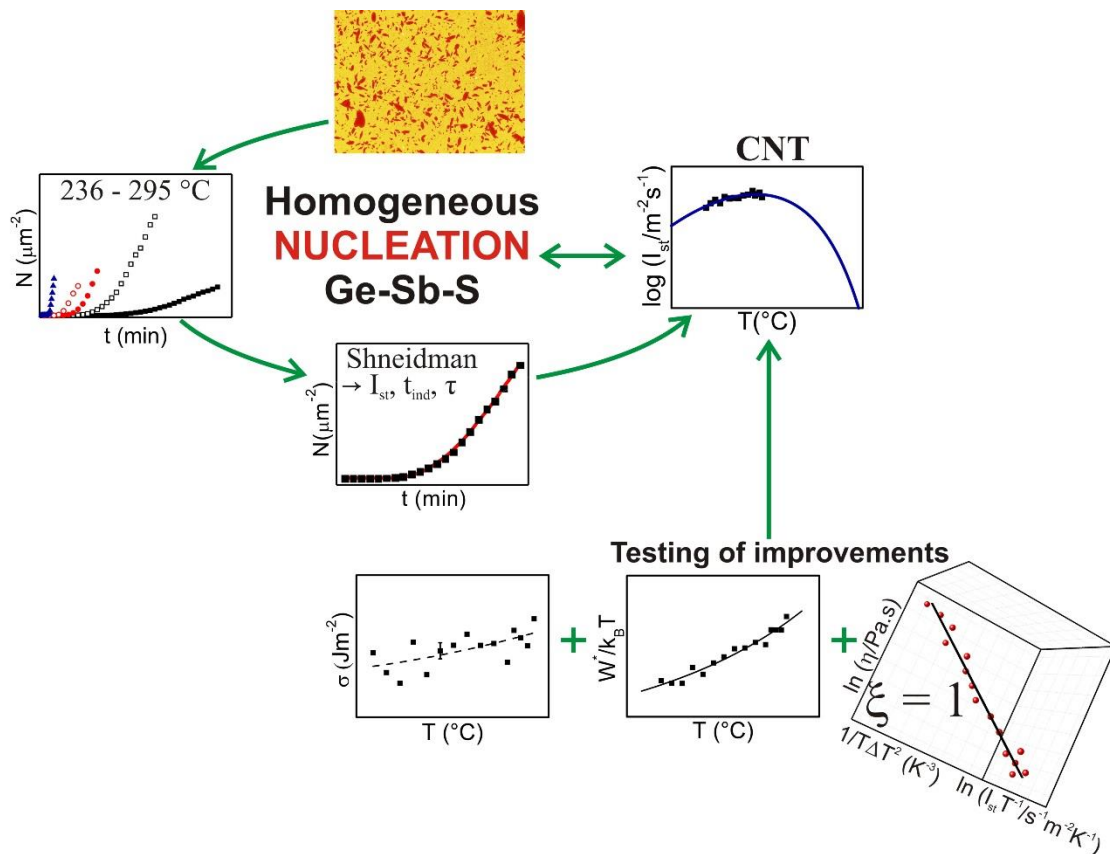


Figure 2: Procedure of the analysis of nucleation in $\text{Ge}_{1.8}\text{Sb}_{36.8}\text{S}_{61.4}$ thin films.

On the basis of our previously published results on crystal growth in the Ge-Sb-S system⁴⁰, where a broad distribution of crystal sizes was observed (Figure 2), the single-stage method was chosen as the appropriate one for the study of nucleation kinetics in these thin films. The crystals in thin films grew from randomly distributed nuclei in the volume of thin film, crystallization was not initiated at the surface and the numbers of grown nuclei increased during the isothermal heat treatment of the sample.

All of the mentioned facts suggest the homogeneous mechanism of nucleation. Time evolutions of nuclei number N for various temperatures revealed non-steady-state (transient) behavior. The $N-t$ curves were fitted using two successful theories for transient nucleation (Collins-Kashchiev^{15,16} and Shneidman¹⁸) to find the quantities characterizing nucleation kinetics (steady-state nucleation rate I_{st} , induction period t_{ind} , time-lag τ). Collins-Kashchiev theory is the most famous and commonly used approach to the treatment of experimental $N-t$ data in silicate glasses. Moreover, the obtained values of I_{st} and τ are in a good agreement with those from numerical calculations¹⁷. Nevertheless, it was shown that Collins-Kashchiev theory is not suitable for the description of transient nucleation in the studied thin films. Better description of $N-t$ data and more realistic values of I_{st} , t_{ind} and τ were achieved using Shneidman theory, which was used for the final calculations.

The study also deals with the suitability of CNT for the description of found temperature dependence of the steady-state nucleation rate so that the nucleation behavior could be described in a wide temperature range (from T_g to T_m). Sometimes it is not possible to measure nucleation in such wide temperature range due to a significant crystal growth at the temperatures where nucleation still occurs, i. e. sample is completely crystallized in a few seconds. It was shown in many studies on silicate glasses that CNT is convenient for description of nucleation, nevertheless, certain problems still persisted in case of several materials, thus various improvements of CNT were proposed. CNT is based on a number of assumptions that do not always have to be valid. One of these assumptions is the validity of the Stokes-Einstein relation for the description of molecular transport in nucleation process near the melting point T_m as well as in highly supercooled liquid down to T_g . Another assumption of CNT is that the crystal-liquid interface energy σ is treated as a macroscopic property with a value equal to that of a planar interface, which is known as capillarity approximation. It is well-known that CNT usually fails in calculation of $I-T$ curve if a constant σ is used, so the temperature-dependent interfacial energies should be employed¹⁰. Third, CNT assumes that the thermodynamic properties of the critical cluster and the evolving macroscopic phase are equivalent. Following that and the validity of capillarity approximation, a monotonic decrease of the thermodynamic barrier for nucleation W^* with decreasing temperature is expected. An anomalous behavior of W^* was observed in silicate glasses, therefore, some additional corrections were introduced⁴¹⁻⁴⁴.

The test of validity of the mentioned assumptions for the studied $\text{Ge}_{1.8}\text{Sb}_{36.8}\text{S}_{61.4}$ thin films was performed. It was revealed that no anomalous behavior of W^* occurs in the studied temperature region and that the Stokes-Einstein relation is fulfilled as well near T_g ($\xi = 1$). The temperature dependence of crystal-liquid surface energy was found with the knowledge of theoretical pre-exponential term of classical nucleation model for homogeneous steady-state nucleation and experimental nucleation rates for various temperatures. The found $\sigma(T)$ dependence was weak and nearly constant. Nevertheless, it was found that the model with incorporated $\sigma(T)$ took the experimental observations into better consideration and satisfactorily described nucleation behavior in a wide temperature range. The result of the study, in the form of normalized nucleation curve along with normalized crystal growth curve, is depicted in Figure 3. The strong overlap, with the maxima at 288 °C for nucleation and 309 °C for crystal growth, was found.

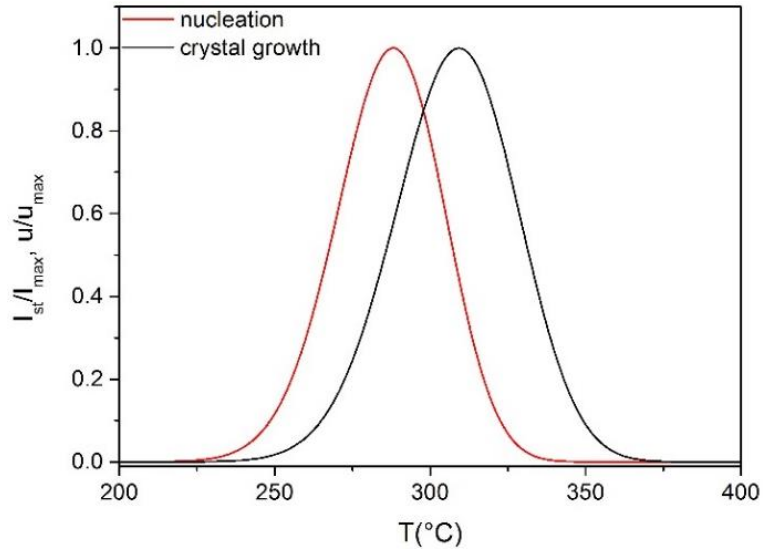


Figure 3: Calculated normalized crystal nucleation and growth curve ($I_{max} = 1.2 \cdot 10^8 \text{ m}^{-2}\text{s}^{-1}$; $u_{max} = 9.9 \cdot 10^{-6} \text{ ms}^{-1}$).

A brief nucleation study in As_2Se_3 bulk glass was performed using TMA, DSC and OM³⁵. This system shows quite complicated surface heterogeneous nucleation process which exhibits stochastic behavior and significantly long time-lags for nucleation (hours to days) in well prepared glass with minimum defects and stresses. Since the nucleation process is heterogeneous, density of formed nuclei can be modified by surface roughness, surface tension, contact with other materials, etc. Somewhat different behavior (shorter time-lag, higher nuclei density, minimized stochastic effects) was observed if the sample was sandwiched between two synthetic sapphire plates in TMA furnace with applied force during the nucleation heat treatment at temperature T_{max} , which corresponds to the maximum nucleation rate according to the study of Holubová et al.⁴⁵. Formed nuclei were visualized by nonisothermal heat treatment in DSC furnace and observed and counted using optical microscope. The finite number of nuclei and nucleation rate at T_{max} were determined. These differences in nucleation behavior should be considered during the preparation of molded lenses used in infrared optical systems where the glass is in contact with another material and under applied force.

3.2 Crystal Growth

The crystal growth studies are focused on the description of crystal growth in a wide temperature range combining experimental data obtained mainly using different direct (OM, SEM) experimental techniques with those from indirect (XRD, DSC, TMA) experimental techniques^{29,31,33,35}.

The first study is focused on the isothermal study of crystal growth in the volume of $\text{Se}_{100-x}\text{Te}_x$ bulk glasses ($x = 10, 20, \text{ and } 30$) using optical microscope equipped with infrared camera³³, which is schematically depicted in Figure 4.

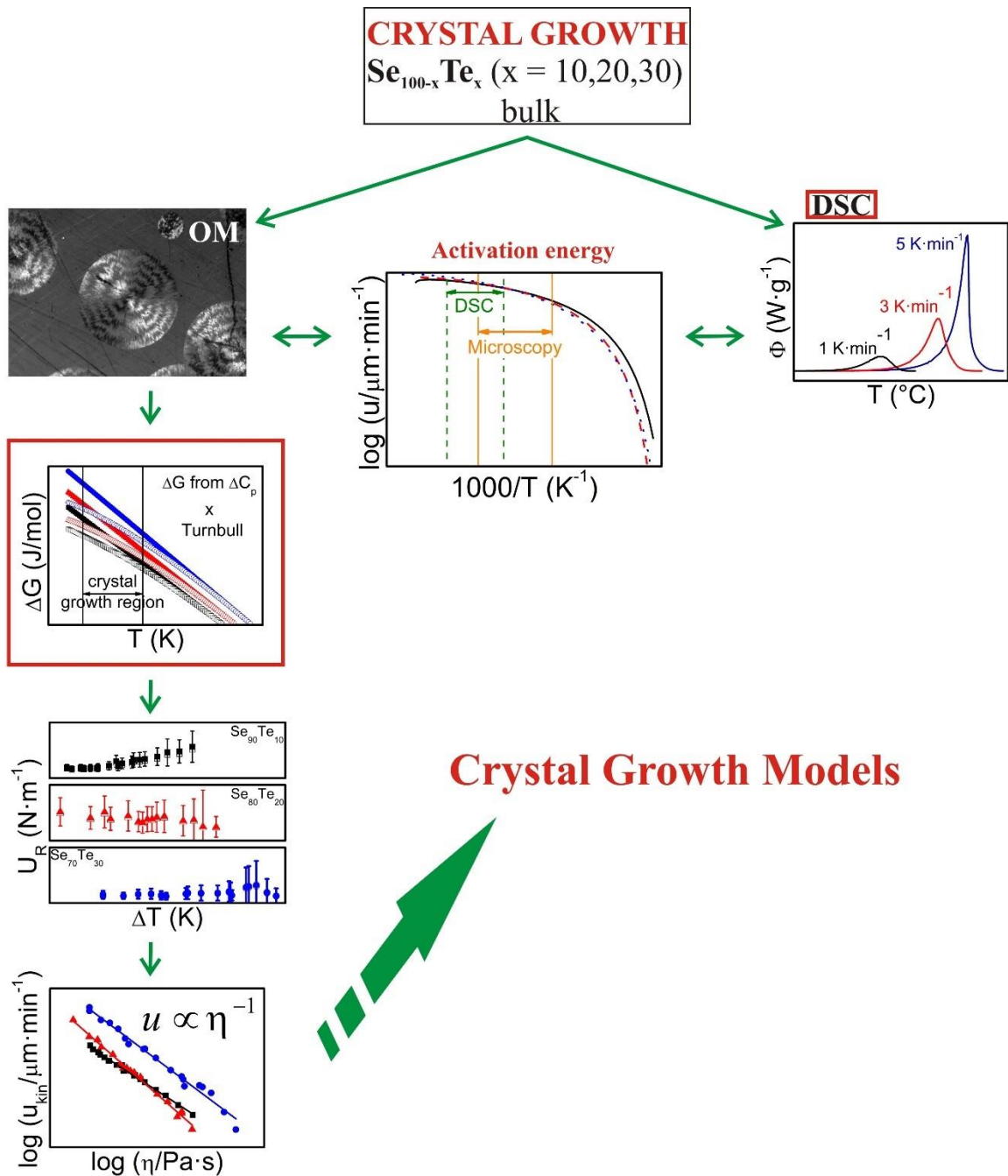


Figure 4: Procedure and highlights of the analysis of crystal growth in $\text{Se}_{100-x}\text{Te}_x$ ($x = 10, 20, 30$) bulk glasses.

With the knowledge of crystal growth data from the microscopy measurements and temperature dependencies of η and ΔG , one can obtain the appropriate crystal growth model. Two different approaches for calculation of ΔG were analyzed in order to examine its influence on the determination of crystal growth model. The change in Gibbs free energy between supercooled liquid and crystalline phase ΔG is most often calculated using the approximation proposed by Turnbull due to the missing heat capacity data for chalcogenide glasses. The heat capacities of the crystalline and supercooled liquid phases are available for the Se-Te system⁴⁶, so ΔG could be calculated using both expressions. It was found that with increasing supercooling the

difference in ΔG calculated using the two approaches occurs. Nevertheless, ΔG can be substituted by simple Turnbull's expression, providing comparable results with respect to the modeling of the reduced crystal growth rate and operative crystal growth model. This is because the viscous flow controls the crystallization process in the region where difference in ΔG is observed. Regarding the decoupling of crystal growth rate and viscosity in the studied Se-Te compositions, the values of the kinetic exponent ξ representing the extent of decoupling are close to one even for such highly fragile system ($m_\eta \approx 76 - 88$). It can be assumed that the Stokes-Einstein relation is fulfilled even at higher undercoolings. An alternative way to study the crystallization process using DSC was also performed. Activation energies of the overall crystallization process evaluated from DSC measurements were compared within the activation energies of crystal growth calculated from the exponential dependence of crystal growth on temperature. One should note that such comparison of the activation energies is meaningful only in the same studied temperature range, because the dependence of $\log u$ on $1/T$ is highly nonlinear in a wider temperature region. Therefore, the activation energies of crystal growth were calculated in the temperature region where the DSC measurements were performed. It was found that this approach brought comparable values of the activation energies, which indicates that the crystal growth is the leading process in the overall crystallization process recorded by DSC, and that nucleation does not take place in the studied temperature region.

The second study of crystal growth deals with the isothermal study of crystal growth kinetics in $\text{Se}_{70}\text{Te}_{30}$ thin films of thicknesses of 1 μm and 520 nm using the infrared and scanning electron microscopes and in situ X-ray diffraction (XRD) measurements (Figure 5)³¹. This work continues in the crystal growth studies in Se-Te thin films⁴⁷. The growth data obtained from the microscopy measurements were combined with the viscosity data and melting parameters, and the appropriate crystal growth model was assessed. It was found that the simple screw dislocation model (suitable according to the first estimation) does not fit the experimental data well because of the breakdown of the Stokes-Einstein relation ($\xi = 0.64$). Taking into account this fact, the correction of the standard growth model by incorporation of kinetic exponent ξ was suggested. This suggestion brought a new insight into the application of standard crystal growth model with respect to the $u - \eta$ relation. Besides the study of crystal growth using the microscopic measurements, another approach to the study of crystallization kinetics was applied. The evolution of crystallization was studied using in situ XRD, which is based on the recording the changes in diffraction peaks during isothermal annealing. The measured crystallization data were interpreted using the Johnson-Mehl-Avrami (JMA) nucleation-growth model⁴⁸⁻⁵¹ which can be expressed by equation:

$$\alpha = 1 - \exp[-(Kt)^m] \quad (13)$$

where α is the crystallized fraction at time t , K is the rate constant and m is the Avrami exponent reflecting the characteristics of nucleation and growth process. The average value of Avrami exponent indicated two-dimensional crystal growth, which was confirmed by direct observations. The results of XRD measurements were compared with the microscopic ones. The similar values of activation energies of the overall crystallization process (XRD) and crystal growth (SEM) can be explained in two ways: nucleation process has been finished and occurs in another temperature region; XRD

technique is quite insensitive towards detecting nuclei and only crystal growth was followed.

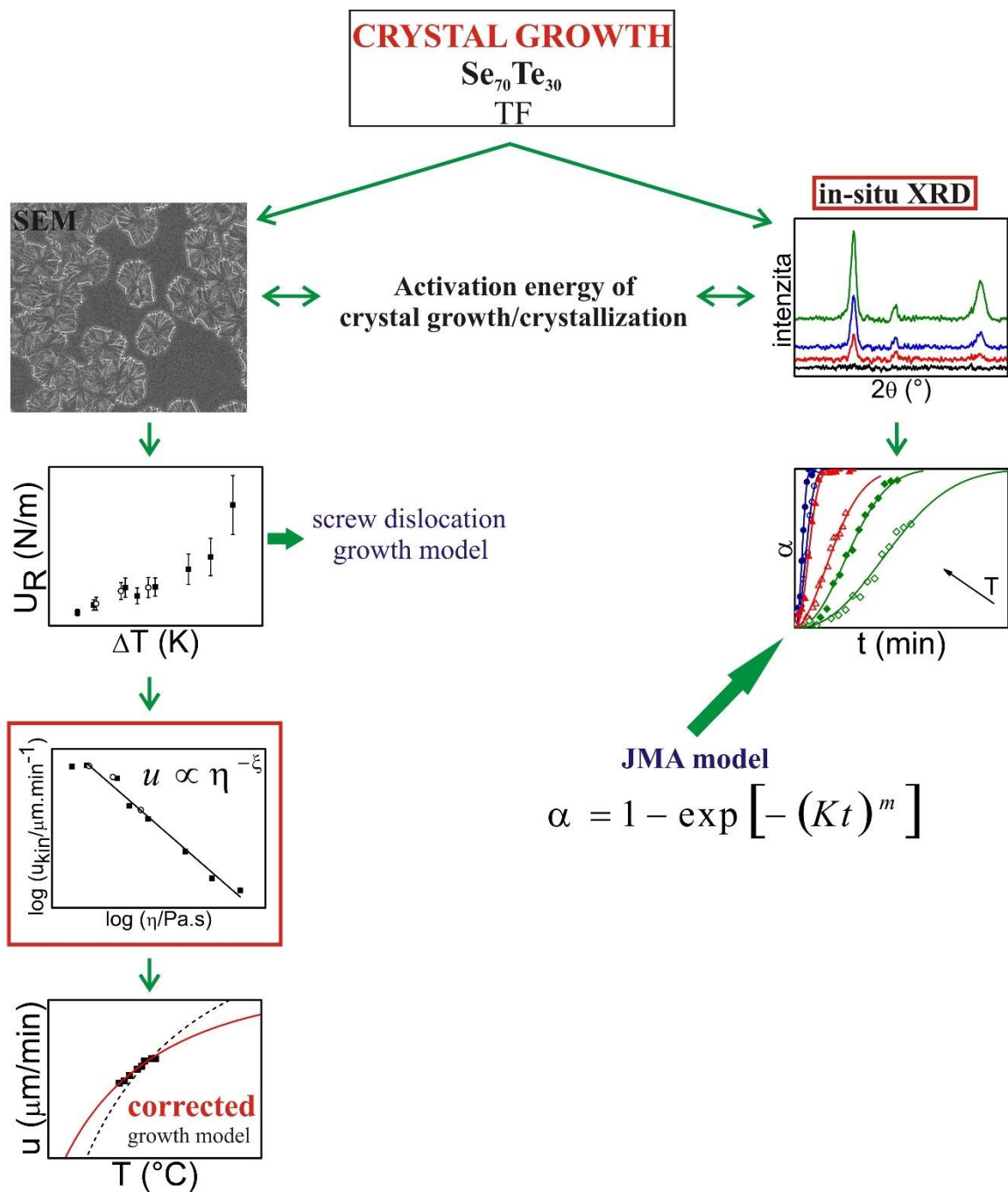


Figure 5: Procedure and highlights of the analysis of crystal growth in $\text{Se}_{70}\text{Te}_{30}$ thin films.

Extended study on crystal growth, melting process, temperature dependence of viscosity and structure of crystalline phase in $\text{Ge}_{18}\text{Sb}_{28}\text{Se}_{54}$ bulk glasses and thin films, which is schematically depicted in Figure 6, was performed. The crystal growth rates in $\text{Ge}_{18}\text{Sb}_{28}\text{Se}_{54}$ bulk glasses and thin films were determined using optical and scanning electron microscopies under isothermal conditions.

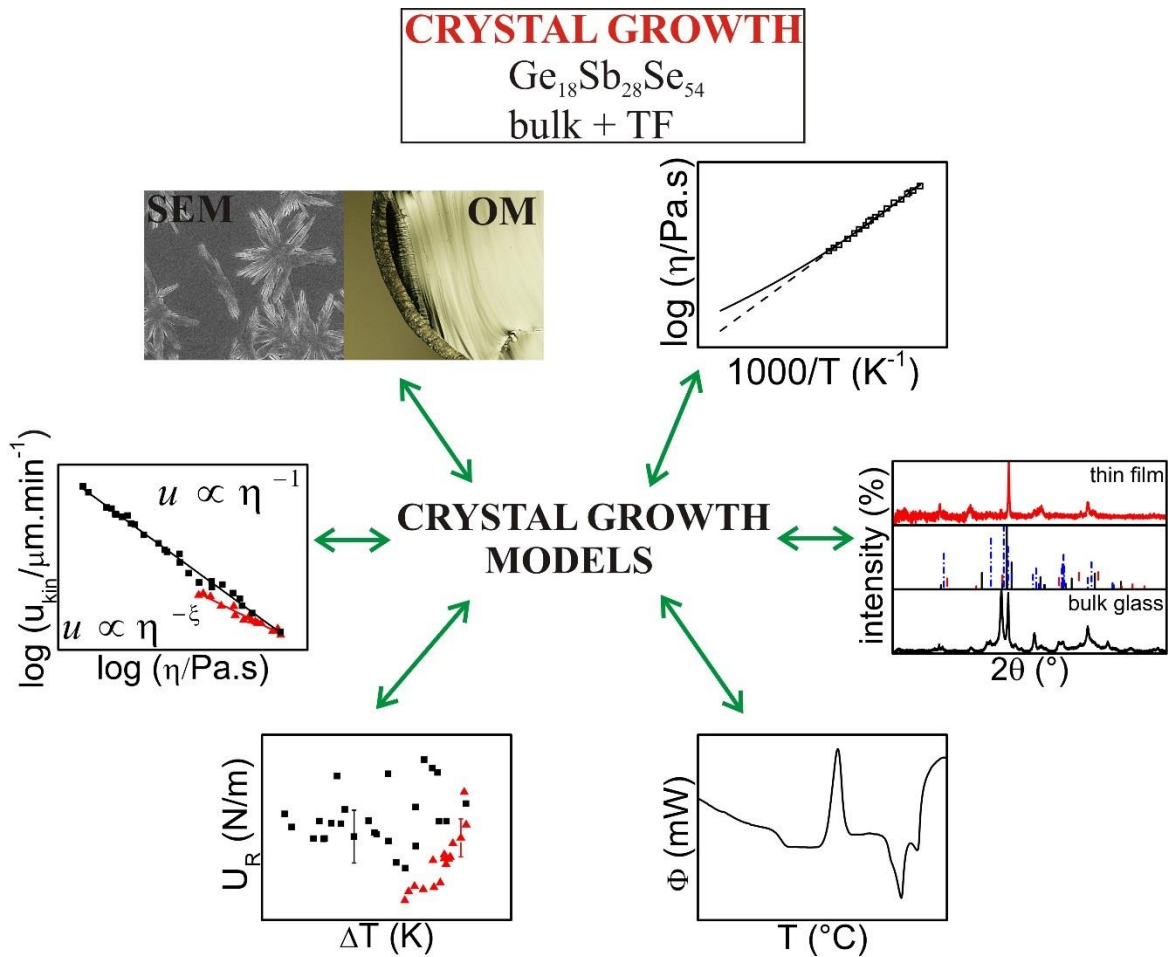


Figure 6: Procedure and highlights of the analysis of crystal growth in $\text{Ge}_{18}\text{Sb}_{28}\text{Se}_{54}$ thin films and bulk glasses.

The compact crystalline layer growing from the surface into the amorphous core and needle-shape crystals were observed in bulk glass and thin films, respectively. The investigation of structure of crystallized bulk sample and thin films performed using XRD together with the measurements of crystallization and melting process of bulk sample performed using DSC under nonisothermal conditions revealed quite complex structure of the formed crystalline phase. With the knowledge of crystal growth, viscosity and melting data, the probable growth models were assessed. Regarding the decoupling of crystal growth rate and viscosity in $\text{Ge}_{18}\text{Sb}_{28}\text{Se}_{54}$ bulk glasses and thin films, similar findings as in Se-Te system (Papers II and III) were observed. Simple proportionality of crystal growth rate to inverse viscosity according to the Stokes-Einstein relation holds for the bulk material ($\xi = 0.98$) and is not fulfilled in the case of thin films ($\xi = 0.67$). Taking into account the possible decoupling, shape of the dependence of U_R on ΔT and previously found results in Ge-Sb-Se system, experimental growth data of bulk glasses and thin films were fitted using two models. Unfortunately, it was not possible to distinguish which model is better for the description of crystal growth in a wide temperature range, because the calculated models differ only in the region close to the melting where the experimental growth data cannot be obtained with the used techniques. Although the appropriate crystal growth model was not found, this

study provides a certain concept of growth behavior in $\text{Ge}_{18}\text{Sb}_{28}\text{Se}_{54}$ bulk glass and thin film.

The last study concerning the crystal growth considerably extends the crystal growth rate data in As_2Se_3 material, which were published by Henderson and Ast⁵², to higher temperatures up to the region close to melting point and completes the findings about the crystal growth behavior in As_2Se_3 bulk glass using optical microscopy and thermoanalytical measurements under isothermal and nonisothermal conditions (see Figure 7)³⁵.

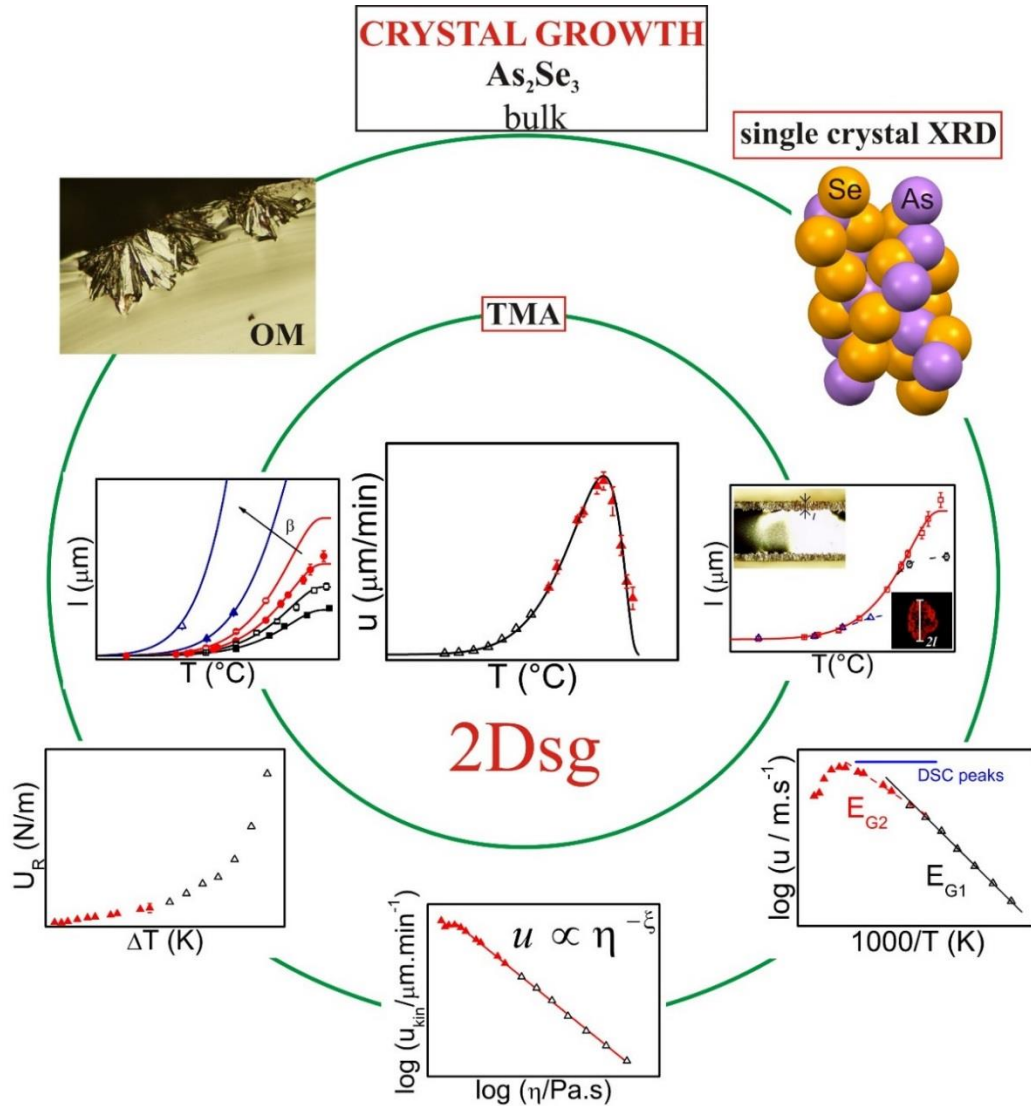


Figure 7: Procedure and highlights of the analysis of crystal growth in As_2Se_3 bulk glass.

This system exhibits only surface crystallization which is quite complicated, heterogeneous and totally stochastic process with significantly long time-lag for nucleation. Therefore, the samples were firstly nucleated to ensure higher nucleation density and make the study of crystal growth possible. It was proved that all isothermal crystal growth rate data can be well described by the kinetic exponent corrected 2D surface nucleated growth model. Regarding the decoupling of crystal growth rate and

viscosity in this system, its extent was tested by three different approaches: Ediger's approach ($\log u_{kin}$ vs $\log \eta$); least square fit of linearized equation for 2D surface nucleated growth model with incorporated ξ in three-dimensional space; and ratio of the activation energy of crystal growth and the activation energy of viscous flow. All ways of testing provided values of kinetic exponent ξ that well correspond to each other within the combined error limits ($\xi = 0.69$). The corrected 2D surface nucleated crystal growth model also successfully describes the development of crystalline layer thickness and growth pattern at amorphous sample surface in nonisothermal conditions. It was shown that one should pay attention to finding of the proper value of melting enthalpy with respect to the difference in values between the crystallization and melting enthalpies, which indicates some uncrystallized amorphous phase in seemingly crystallized sample. Fully crystallized ingot of As_2Se_3 was prepared in a special way in order to find the proper melting enthalpy and examination of single crystal structure. Furthermore, the difficulty to obtain reliable values of ΔC_p due to the sublimation of crystalline As_2Se_3 and the volatility of its liquid was clearly demonstrated. This can be observed in many chalcogenide glassy systems and hence the approximations for ΔG calculation are applied.

The crystal growth studies presented in the doctoral dissertation were performed in various chalcogenide glassy systems in the form of bulk glasses or thin films using many direct and indirect techniques. One of the important links between these studies was the relation of crystal growth and viscous flow with respect to their decoupling. Ediger et al.²³ demonstrated for numerous organic and inorganic glasses that the exponent ξ is linearly correlated with fragility m_η of the system: $\xi = 1.1 - 0.005 \cdot m_\eta$. Figure 8, which shows the dependence of exponent ξ on fragility m_η for the studied chalcogenide glasses, suggests that Ediger's relation might not be generally valid, especially in the case of chalcogenide glasses since they do not practically show any dependence of decoupling on fragility.

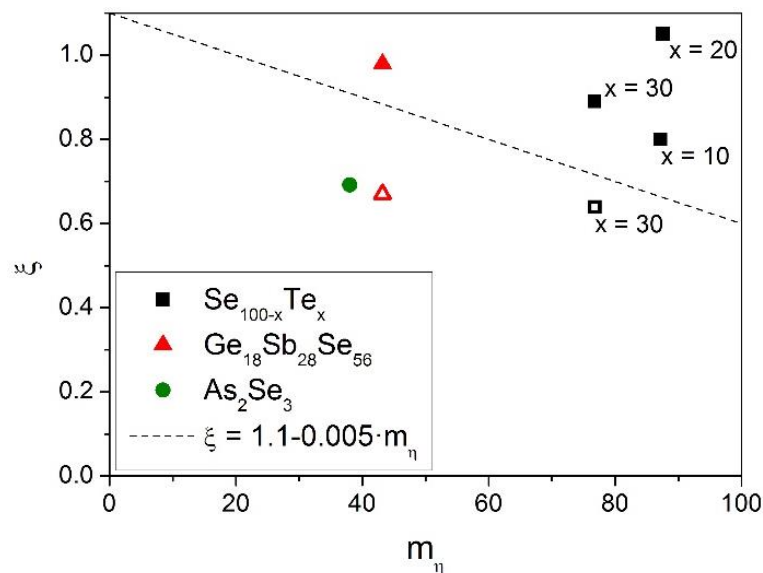


Figure 8: Dependence of kinetic exponent ξ expressing the extent of decoupling between crystal growth rate and viscous flow on fragility m_η of system for various

chalcogenide systems; solid symbols correspond to bulk glass, empty symbols correspond to thin film.

It can be concluded that Ediger's assumption does not hold for chalcogenide glasses and it is necessary to deal with the viscosity-growth relation individually in every single study.

4. Conclusions

Nucleation in chalcogenide glasses – the first aim of the doctoral thesis was to study nucleation kinetics and test the applicability of CNT and of its improvements for description of the steady-state nucleation and analysis of transient models for nucleation in chalcogenide glassy systems.

Experiments and findings:

- Nucleation in $\text{Ge}_{1.8}\text{Sb}_{36.8}\text{S}_{61.4}$ thin films of thickness 1 μm (isothermal in-situ single-stage annealing; optical microscope coupled with heating stage)
- Change of N with annealing time and temperature, crystals grew from randomly distributed nuclei in volume of the thin film \rightarrow signs of homogeneous nucleation mechanism
- Non-steady state behavior described using Shneidman theory \rightarrow values of I_{st} , t_{ind} , τ
- Test of CNT assumptions validity such as validity of the Stokes-Einstein relation for the description of molecular transport in nucleation process, capillarity approximation, and equality of thermodynamic properties of the critical cluster and the evolving macroscopic phase
- Incorporation of appropriate corrections of CNT into the model \rightarrow satisfactory description of the temperature dependence of steady-state nucleation rates, description of nucleation behavior in $\text{Ge}_{1.8}\text{Sb}_{36.8}\text{S}_{61.4}$ thin films in a wide temperature range
- Direct observations \rightarrow nucleation in chalcogenide glasses occurs mostly at sample surface via heterogeneous mechanism \rightarrow in most cases only qualitative data on nucleation
- Further investigations are necessary to achieve any general conclusion

Crystal Growth in chalcogenide glasses – the second aim of the doctoral thesis was to study crystal growth using mainly direct microscopy techniques in order to obtain further information about crystal morphologies, crystal growth behavior and kinetics for selected chalcogenide glasses.

Experiments and findings:

- Studies of chalcogenide glassy systems in the form of bulk glass or thin film: Se-Te, Ge-Sb-Se, As_2Se_3
- Mostly direct observations of crystal growth using microscopy technique – obtaining the information about crystal growth rates and morphology of formed crystals
- Joint objective of the presented papers – description of crystal growth behavior in a wide temperature range combining experimental results and growth models

- Discussion about the proportionality of crystal growth rate to viscosity, which was tested in various ways
- Verification of general validity of the Ediger's correlation between the kinetic exponent and fragility → relation does not hold for chalcogenide glasses
- Breakdown of Stokes-Einstein relation (mostly observed in thin films) → correction of standard growth models via incorporation of the kinetic exponent
- Activation energies of the overall crystallization process (from DSC) and activation energies of the crystal growth (from microscopic measurements) – only comparison in the same temperature range is meaningful
- Study of structure and melting parameters – obtaining the proper values
- Test of calculating ΔG using heat capacity data and using approximations → comparable results regarding the modeling of reduced crystal growth rate and operative crystal growth model
- Obvious necessity of combining direct and indirect techniques for crystallization studies in order to get reliable detailed results on the crystallization process

The presented thesis contains extended study of nucleation in chalcogenide glasses, providing not only the qualitative description of nucleation behavior in the studied system, but also the quantitative results, which are quite unique. As far as we know, most studies of nucleation in chalcogenide glasses are only qualitative. With the knowledge of nucleation rate data, the test of suitability of famous classical nucleation theory (CNT) and its improvements was performed. It was found that CNT is sufficient for the description of nucleation behavior in a wide temperature range in the studied chalcogenide glass, nevertheless it has to be noted realize that more studies on nucleation kinetics in different chalcogenide glasses are necessary to be able to make a general conclusion.

Regarding the crystal growth, this systematic work yields further findings in description of crystal growth behavior. The presented results extend the knowledge of the effect of $u - \eta$ relation on the description of crystal growth data using growth models. In the case of decoupling between u and η , the standard growth models can be modified by incorporation of the kinetic exponent ξ , which leads to a better description of experimental growth data. It was found that there is no simple general formula connecting the decoupling with fragility for chalcogenide glasses. Using the combination of results from classic microscopic studies with those of macroscopic ones, detailed and interesting information about crystallization process as a whole is obtained, and therefore more detailed understanding of crystallization process can be achieved.

List of References

- 1 N. Mehta, J. Sci. Ind. Res. **65**, 777-786 (2006).
- 2 M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200-13212 (1996).
- 3 E. D. Zanutto and J. C. Mauro, J. Non-Cryst. Solids **471**, 490-495 (2017).
- 4 K. F. Kelton and A. L. Greer, *Nucleation in Condensed Matter: Applications in Materials and Biology*. (Pergamon, 2010), pp.1-743.
- 5 D. R. Uhlmann and B. Chalmers, Ind. Eng. Chem. **57**, 19-31 (1965).
- 6 D. Turnbull, J. Appl. Phys. **21**, 1022-1028 (1950).
- 7 C. V. Thompson and F. Spaepen, Acta Metall. **27**, 1855-1859 (1979).
- 8 H. B. Singh and A. Holz, Solid State Commun. **45**, 985-988 (1983).
- 9 J. D. Hoffman, J. Chem. Phys. **29**, 1192-1193 (1958).
- 10 P. F. James, J. Non-Cryst. Solids **73**, 517-540 (1985).
- 11 I.S. Gutzow and J.W.P. Schmelzer, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*. (Springer, 2013).
- 12 Ya B. Zeldovich, Acta Physicochim., USSR **18**, 1-22 (1943).
- 13 J. W. P. Schmelzer, A. S. Abyzov, and V. G. Baidakov, Int. J. Appl. Glass Sci. **8**, 48-60 (2017).
- 14 K. F. Kelton, Solid State Phys. **45**, 75-177 (1991).
- 15 F. C. Collins, Z. Elektrochem. **59**, 404-407 (1955).
- 16 D. Kashchiev, Surf. Sci. **14**, 209-220 (1969).
- 17 K. F. Kelton, A. L. Greer, and C. V. Thompson, J. Chem. Phys. **79**, 6261-6276 (1983).
- 18 V. A. Shneidman, Zhurnal Tek. Fiz. **58**, 2202-2209 (1988).
- 19 M. L. F. Nascimento and E. D. Zanutto, J. Chem. Phys. **133**, 174701-1 - 174701-10 (2010).
- 20 R.J. Kirkpatrick, Am. Mineral. **60**, 798-814 (1975).
- 21 K. A. Jackson, D. R. Uhlmann, and J. D. Hunt, J. Cryst. Growth **1**, 1-36 (1967).
- 22 K. L. Ngai, J. H. Magill, and D. J. Plazek, J. Chem. Phys. **112**, 1887-1892 (2000).
- 23 M. D. Ediger, P. Harrowell, and L. Yu, J. Chem. Phys. **128**, 034709-1 - 034709-6 (2008).
- 24 M. L. F. Nascimento, E. B. Ferreira, and E. D. Zanutto, J. Chem. Phys. **121**, 8924-8928 (2004).
- 25 M. L. F. Nascimento and E. D. Zanutto, Phys. Rev. B **73**, 024209-1 - 024209-7 (2006).
- 26 M. L. F. Nascimento, V. M. Fokin, E. D. Zanutto, and A. S. Abyzov, J. Chem. Phys. **135**, 194703-1 - 194703-17 (2011).
- 27 J. W. P. Schmelzer, A. S. Abyzov, V. M. Fokin, C. Schick, and E. D. Zanutto, J. Non-Cryst. Solids **429**, 45-53 (2015).
- 28 J. W. P. Schmelzer, A. S. Abyzov, V. M. Fokin, C. Schick, and E. D. Zanutto, J. Non-Cryst. Solids **428**, 68-74 (2015).
- 29 S. Martinkova, J. Bartak, P. Kostal, J. Malek, and H. Segawa, J. Phys. Chem. B **121**, 7978-7986 (2017).
- 30 J. Malek, J. Bartak, and J. Shanelova, Cryst. Growth Des. **16**, 5811-5821 (2016).
- 31 S. Martinkova, J. Bartak, J. Malek, and H. Segawa, J. Appl. Phys. **120**, 145301-1 - 145301-7 (2016).

- 32 S. C. Glotzer, *J. Non-Cryst. Solids* **274**, 342-355 (2000).
- 33 Jaroslav Bartak, Simona Martinkova, and Jiri Malek, *Cryst. Growth Des.* **15**,
4287-4295 (2015).
- 34 S. Martinkova, J. Shadelova, J. Bartak, and J. Malek, *Cryst. Growth Des.* **18**,
4562-4570 (2018).
- 35 J. Malek, J. Shanelova, S. Martinkova, P. Pilny, and P. Kostal, *Cryst. Growth
Des.* **17**, 4990-4999 (2017).
- 36 S. K. Pillai and J. Malek, *J. Mater. Sci.* **50**, 3854-3859 (2015).
- 37 G. K. Johnson, G. N. Papatheodorou, and C. E. Johnson, *J. Chem. Thermodyn.*
13, 745-754 (1981).
- 38 Jana Shánělová, Petr Košťál, and Jiří Málek, *J. Non-Cryst. Solids* **352**, 3952-
3955 (2006).
- 39 S. K. Pillai, V. Podzemna, J. Bartak, and J. Malek, *J. Cryst. Growth* **382**, 87-93
(2013).
- 40 J. Bartak, V. Podzemna, J. Malek, G. Eising, and B. J. Kooi, *J. Non-Cryst. Solids*
410, 7-13 (2015).
- 41 V. M. Fokin, A. S. Abyzov, E. D. Zanotto, D. R. Cassar, A. M. Rodrigues, and
J. W. P. Schmelzer, *J. Non-Cryst. Solids* **447**, 35-44 (2016).
- 42 J. W. P. Schmelzer and A. S. Abyzov, *J. Non-Cryst. Solids* **449**, 41-49 (2016).
- 43 A. S. Abyzov, V. M. Fokin, A. M. Rodrigues, E. D. Zanotto, and J. W. P.
Schmelzer, *J. Non-Cryst. Solids* **432**, 325-333 (2016).
- 44 A. S. Abyzov, V. M. Fokin, N. S. Yuritsyn, A. M. Rodrigues, and J. W. P.
Schmelzer, *J. Non-Cryst. Solids* **462**, 32-40 (2017).
- 45 J. Holubova, Z. Cernosek, and E. Cernoskova, *J. Therm. Anal. Calorim.* **114**,
997-1002 (2013).
- 46 R. Svoboda and J. Malek, *J. Chem. Phys.* **141**, 224507-1 - 224507-10 (2014).
- 47 J. Barták, J. Málek, P. Košťál, H. Segawa, and Y. Yamabe-Mitarai, *J. Appl. Phys.*
115, 123506-1 - 123506-7 (2014).
- 48 W. A. Johnson and R. F. Mehl, *Trans. Aime* **135**, 416-458 (1939).
- 49 M. Avrami, *J. Chem. Phys.* **9**, 177-184 (1941).
- 50 M. Avrami, *J. Chem. Phys.* **7**, 1103-1112 (1939).
- 51 M. Avrami, *J. Chem. Phys.* **8**, 212-224 (1940).
- 52 D. W. Henderson and D. G. Ast, *J. Non-Cryst. Solids* **64**, 43-70 (1984).

List of Published Works

Paper I

MARTINKOVÁ, Simona, SHÁNĚLOVÁ, Jana, BARTÁK, Jaroslav, MÁLEK, Jiří. Transient Nucleation in Ge-Sb-S Thin Films. *Crystal Growth and Design*, 2018, 18, 4562 – 4570.

Paper II

BARTÁK, Jaroslav, MARTINKOVÁ, Simona, MÁLEK, Jiří. Crystal Growth Kinetics in Se-Te Bulk Glasses. *Crystal Growth and Design*, 2015, 15, 4287 – 4295.

Paper III

MARTINKOVÁ, Simona, BARTÁK, Jaroslav, MÁLEK, Jiří, SEGAWA, Hiroyo. Crystal Growth in $\text{Se}_{70}\text{Te}_{30}$ Thin Films Followed by SEM and In Situ XRD. *Journal of Applied Physics*, 2016, 120, 145301-1 – 145301-7.

Paper IV

MARTINKOVÁ, Simona, BARTÁK, Jaroslav, KOŠŤÁL, Petr, MÁLEK, Jiří, SEGAWA, Hiroyo. Extended Study on Crystal Growth and Viscosity in Ge-Sb-Se Bulk Glasses and Thin Films. *Journal of Physical Chemistry B*, 2017, 121, 7978 – 7986.

Paper V

MÁLEK, Jiří, SHÁNĚLOVÁ, Jana, MARTINKOVÁ, Simona, PILNÝ, Petr, KOŠŤÁL, Petr. Crystal Growth Velocity in As_2Se_3 Supercooled Liquid. *Crystal Growth and Design*, 2017, 17, 4990 – 4999.