

AN ABSTRACT OF THE THESIS OF

Mark M. Winseck for the degree of Master of Science in Materials Science presented on December 14, 2017.

Title: Characterization of Low Temperature Crystallization Growth Parameters of the Growth-dominated Phase Change Materials: $\text{Ge}_1\text{Sb}_6\text{Te}_1$ and $\text{Ga}_{15}\text{Sb}_{85}$ by Optical Microscopy

Abstract approved:

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Phase change memory materials are a set of chalcogenide or pnictogenide materials systems currently being researched for use in optical and resistive based memory systems due to their large change in optoelectronic properties between the amorphous and the crystalline states. For these materials systems to be considered as a suitable candidate for memory applications it is imperative that crystal growth characteristics are understood across a range of temperatures. It is necessary for these materials to have low crystallization rates at lower temperatures so that the written memory remains stable for a prolonged period of time. In this work, the low temperature crystal growth rate and Johnson Mehl Avrami Kolmogorov analysis parameters of two growth-dominated phase change material systems, GeSb_6Te and $\text{Ga}_{15}\text{Sb}_{85}$, were calculated using in-situ hot stage optical microscopy. GeSb_6Te was isothermally crystallized at temperatures from 185°C to 195°C and $\text{Ga}_{15}\text{Sb}_{85}$ was isothermally crystallized at temperatures 170°C to 180°C. Images were taken and the growth of individual grains was measured as well as the percent of material crystallized. These materials were found to have comparable growth and crystallization rates in the low temperature region as other typical nucleation-dominated materials such as Ag- and In- doped Sb_2Te and GeTe . The measurements done in this work are part of a broader goal to characterize the crystallization kinetics of phase change materials systems over the entire range of temperatures where crystallization occurs.

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Characterization of Low Temperature Crystallization Growth Parameters of the Growth-dominated
Phase Change Materials: $\text{Ge}_1\text{Sb}_6\text{Te}_1$ and $\text{Ga}_{15}\text{Sb}_{85}$ by Optical Microscopy

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Mark M. Winseck, Author

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LIST OF ACRONYMS AND SYMBOLS

Acronym or Symbol	Meaning
A	Time dependence of number of nuclei
a_0	Interatomic distance
AFM	Atomic force microscopy
AIST	Ag- In- doped Sb_2Te
b	Dimensionality of crystal growth
BD-RE	Rewritable Blue-Ray disc
c	Diffusion or interfacial growth constant
CD-RW	Rewritable CD format
D	Diffusion coefficient
DSC	Differential scanning calorimetry
DTEM	Dynamic transmission electron microscopy
DVD-RW	Rewritable DVD format
E_{comb}	JMAK activation energy
E_g	Activation energy of crystal growth
E_{nuc}	Activation energy of nucleation
EDS	Energy dispersive spectroscopy
GST	Germanium antimonide telluride alloy
GST161	$Ge_1Sb_6Te_1$
GST225	$Ge_2Sb_2Te_5$
h	Planck's constant
I	Nucleation rate
I_0	Nucleation rate pre-exponential constant
JMAK	Johnson-Mehl-Avrami-Kolmogorov analysis
k	JMAK crystallization rate
k_0	JMAK crystallization pre-exponential constant
k_B	Boltzmann's constant

LIST OF ACRONYMS AND SYMBOLS (Continued)

n	Avrami exponent
N	Number of nuclei
PCM	Phase change memory material
r^*	Critical nuclei radius
t	Time
t_{inc}	Incubation time
$t_{\text{xtallization}}$	Time to erase an amorphous mark
T	Temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{max}	Temperature at which maximum crystal growth occurs
T_x	Crystallization temperature
U	Crystal growth velocity
U_0	Crystal growth pre-exponential constant
U_{max}	Maximum crystal growth velocity
γ	Interfacial energy
ΔG^*	Thermal barrier to nucleation
ΔG_v	Difference in Gibbs free energy of phases involved in phase transition
η	Viscosity
λ	Atomic jump distance
ν	Vibrational frequency
τ	Relaxation time for transient nucleation
χ	Fraction of material crystallized

1. Introduction

Phase change memory materials (PCMs) are a set of glass-forming alloys that are defined by their ability to switch between two different phases that have contrasting optical and electronic properties. PCMs are used as memory materials where the crystalline to amorphous melt-quench operation is considered the write function and the regrowth of the crystalline phase is considered the rewrite operation (the amorphous phase and the crystalline phase represent 1's and 0's, respectively). Currently, PCMs have found use in rewritable optical disks such as rewritable CDs, DVDs, and Blue Ray discs.¹ Considerable research has gone into finding new phase change materials to be used in both optical discs, as well as, for use in Joule-heating based random access memory.² PCMs are divided into two groups based on their crystallization characteristics: nucleation-dominated materials and growth-dominated materials. This work focuses on the growth-dominated materials $\text{Ge}_1\text{Sb}_6\text{Te}_1$ and $\text{Ga}_{15}\text{Sb}_{85}$ and the characterization of their crystallization parameters at low temperatures using in-situ optical microscopy. This work is part of an overarching goal to use microscopy techniques to directly measure crystal growth rates over a larger range of temperatures.

2. Background

2.1. Phase Change Materials (PCMs)

2.1.1. Electrical and Optical Properties of Phase Change Materials

A major criterion for a system to be considered a good candidate for use as a phase change memory material is that there must be a significant change in either the optical or electrical properties of the system upon phase transformation. In most phase change materials, the crystallization of the amorphous phase is accompanied by an increase in the optical reflectance and a decrease in the electrical resistivity.³ Current optical disk requirements specifically require that there needs to be a noticeable difference of reflectivity of a blue laser light. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) currently is used because it has good optical contrast of around 20% difference in reflectivity⁴. A significant difference in electrical resistivity is usually considered to be a change of several orders of magnitude resistance.

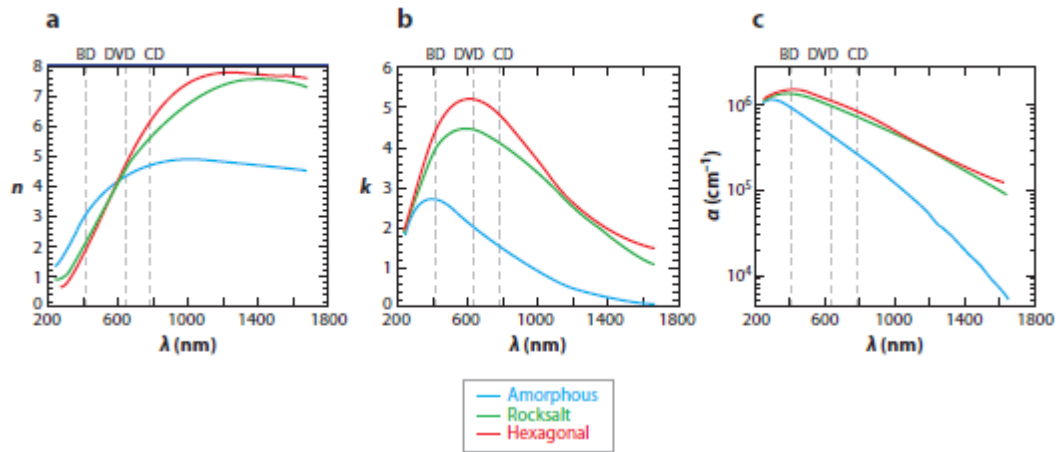


Figure 1 a) refractive index, b) extinction coefficient, and c) absorption coefficient of GST225 as a function of wave length of light.⁵

The change in reflectivity is caused by a decrease in optical band gap upon crystallization.⁶ For GST225 the optical band gap of the amorphous phase is 0.7 eV and for the crystalline phase it is ~ 0.5 eV.⁵ The change in optical constants upon crystallization are shown in Figure 1. These optical constants are also dependent on film thickness as well as wavelength. The maximum refractive index, extinction coefficient and absorption coefficient all increase upon crystallization. The wavelength of these maximums also shifts to a longer wavelength upon crystallization from a wavelength in the blue-violet region to one that is farther into the visible spectrum.⁵

2.1.2. Crystallization Kinetics of Phase Change Materials

To be considered an adequate phase change material several criteria must be met in regards to the crystallization characteristics of the material. The first criterion that must be met is that there must be a high crystallization rate at high temperatures.⁷ This is necessary to maintain fast rewrite-speeds. The melt-quench transition rate to the amorphous phase is independent of the material system so the rewrite speed is the critical differentiating process when it comes to write-rewrite speed.

In addition to requiring a fast high temperature growth, phase change materials also require a slow low temperature growth. This is critical for long-term stability of the data. If the low temperature growth rate is too quick, then it is possible that the amorphous marks will be erased at operating temperatures. The crystallization temperature, T_x , is a parameter used to

evaluate low-temperature growth and is defined generally as the temperature at which kinetics are fast enough to allow for crystallization on a reasonable time scale. This temperature is calculated using a DSC and the temperature is dependent on the heating rate used.

Due to the requirements of a fast high temperature growth and a slow low temperature growth, as well as, the fact that when amorphising it is necessary that there is no crystalline growth, it is vitally important to characterize the crystal growth rate of phase change materials from low temperatures all of the way up to the melting temperature.

Another important aspect of the crystallization kinetics of phase change materials is that it is necessary to avoid phase separation upon crystallization. If the material phase separates, the two new phases may have differences in chemical composition that can cause chemical segregation which, over the course of several write-rewrite cycles, may cause changes in the crystal growth rate and melting temperature of the alloy.

2.1.3. Compositions of Phase Change Materials

Phase change materials are based on semiconducting systems. Being semiconducting is a major advantage because dielectric materials tend to be transparent to the wavelength of laser used to melt and crystallize the system. Additionally, metallic glasses do not change optical and electronic properties upon crystallization. Of the semiconducting materials, Group IV elements generally form a diamond crystal structure which results in strong four-coordinated covalent bonds in the crystal structure. This results in a high melting temperature for systems based on these elements. This is an undesirable characteristic in PCMs as it means it is difficult to melt-quench these materials into an amorphous state. In addition, the amorphous forms of Group IV based semiconductors have slow diffusion rates which inhibit the crystallization of the new phase. Excluding Group IV semiconductors the remaining potential semiconducting systems are either based on Group V elements (As and Sb) or Group VI elements (Se and Te).⁸

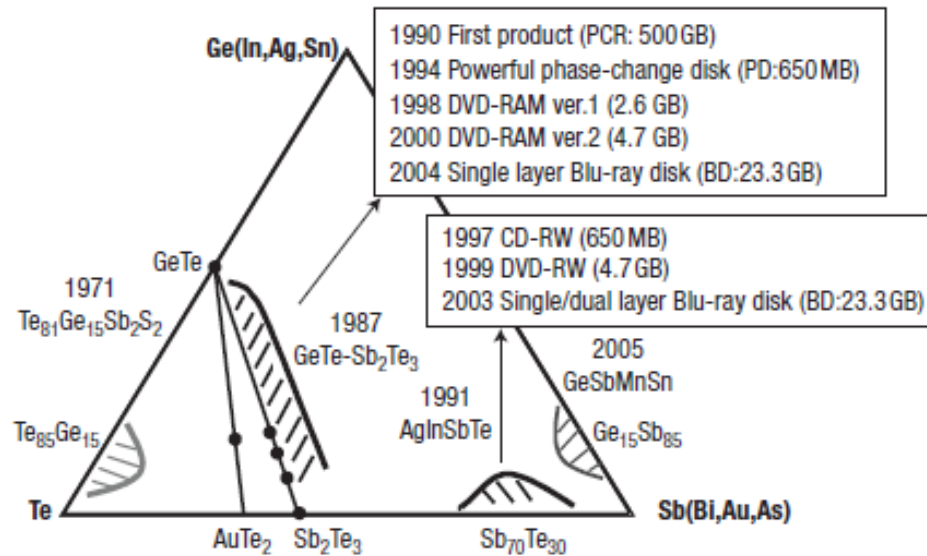


Figure 2: Main PCM alloy families.⁹

Of these systems those based on tellurium and more specifically germanium antimonide telluride (GST) alloys form the largest number of materials that have been researched.⁸ The most common PCM alloy families are shown in Figure 2. Most GST alloys that have been considered for PCM applications fall along the GeTe-Sb₂Te₃ tie line. The alloys on this tie line all have a metastable distorted rock salt structure that incorporates a large number of vacancies.³ This high vacancy structure allows for the structure to be stable or metastable across a wide range of compositions with more vacancies being incorporated into higher Sb₂Te₃ concentration alloys.¹⁰ Most of the materials on this tie line are considered “nucleation-dominated materials” which will be discussed in a later section. Materials on the Sb₂Te₃ end of the tie line crystallize easily but suffer from a small change in reflectivity. In contrast, alloys near the GeTe end of the tie line tends to have great optical contrast properties but worse growth characteristics than Sb₂Te₃. Ge₂Sb₂Te₅ is the tie line composition that has had the most research and industry applications to this point due to its ability to balance the advantages of GeTe’s optical properties with Sb₂Te₃’s fast growth.¹¹

Antimony based systems have also been an area of research as antimony undergoes explosive crystallization,¹² however pure antimony is not stable in the amorphous phase at room temperature. To increase the crystallization temperature antimony is often alloyed with other

elements such as germanium, tellurium, silver, indium, and gallium.⁷ These high antimony systems are generally considered to be growth-dominated materials as their nucleation rate does not play a significant role in the rewrite process. $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ is the most researched and utilized growth-dominated material but research has also gone into high antimony GST alloys as well as gallium antimonide.¹³⁻²⁰

2.1.4. Characterization of Crystallization Parameters

Crystallization of amorphous materials is governed by both kinetic barrier and thermodynamic driving forces. The thermodynamic driving force is the change in free energy in forming a crystal and, for temperatures far below the melting temperature, are very favored towards crystallization, but as the temperature approaches T_m , the driving force decreases. Kinetics limit phase transformations at lower temperatures due to the lack of mobility of atoms in the material. The kinetics increase as temperature increases.²¹ The interplay between the kinetics and thermodynamic driving forces give rise to the three temperature regimes discussed in this section. The low-temperature regime occurs at approximately 40% of the melting temperature or around T_x where the thermodynamic driving force is so great that kinetics can be considered the sole factor that limits crystallization and an Arrhenius relationship can be derived. The intermediate temperature region occurs between approximately 50% and 75% of the melting temperature and is where both kinetics and thermodynamic driving forces affect the crystallization rate of the material. In addition, the kinetics in this region may diverge from the Arrhenius relationship due to reduced viscosity caused by the glass transition. The high temperature regime is located from the temperature of maximum crystal growth to about 95% of the melting temperature and is where thermodynamic driving force plays a large role in the crystallization rate.

By measuring crystallization rates at different temperatures or heating rates the activation energy of the crystallization can be determined. This is done because using the activation energy and the pre-exponential constant crystallization rates can be extrapolated for temperatures around operating conditions. The methods used to measure low-temperature crystallization parameters can be divided into two distinct subsets: those that measure the percent of material crystallized as a function of time and combine the contributions of nucleation and growth into one rate with one activation energy and those that measure the individual contributions of both the nucleation of new crystallites and the growth of existing grains. The first category uses

techniques that measure the overall percent conversion of amorphous material to crystalline using techniques such as differential scanning calorimetry (DSC)²², electrical impedance^{18, 23-24}, or optical reflectance.²⁵⁻²⁷ These methods are either done isothermally at multiple temperatures and Johnson Mehl Avrami Kologorov (JMAK) analysis is used to determine the pre-exponential constant, k_0 , and combined activation energy, E_{comb} , or are done at multiple constant heating rates and Kissinger analysis is used to determine the same parameters.²⁸

The second category uses direct methods of measuring crystal size and number to calculate growth and nucleation rates independently and will consequently yield an activation energy for both nucleation and crystal growth. These methods involve microscopy techniques, most commonly light microscopy,²⁹⁻³¹; atomic force microscopy (AFM),^{15, 28, 31}; or transmission electron microscopy (TEM).^{14, 32-33} The direct methods are always used isothermally at multiple temperatures.

2.1.4.1. Temperature Ranges of Crystallization Characterization Techniques

Each characterization technique is only valid for a certain range of temperatures due to spatial and temporal resolution limitations. All the techniques mentioned can be used at or around the crystallization temperature of the material being studied (approximately 40% of the melting temperature of the material). In addition, ultrafast DSC (heating rates of thousands of degrees Kelvin per second) can be used to calculate combined kinetics parameters for temperatures ranging between 50%-75% of the melting temperature.³⁴⁻³⁶ The maximum end of this range is just below the temperature at which the growth rate is at a maximum. Dynamic TEM (DTEM) is a relatively new technique that can be used to measure growth rates just above the maximum crystal growth rate to about 95% of the melting temperatures.^{37 38}

2.1.5. Nucleation-dominated Versus Growth-dominated Materials

As stated previously phase change memory materials are divided up into two separate groups based on crystallization kinetics: nucleation-dominated materials and growth-dominated materials. Many alloys on the GeTe-Sb₂Te₃ pseudo-binary are nucleation-dominated materials. Typical nucleation-dominated growth appears in Figure 3. The dark purple phase is the crystalline material and the light green is amorphous. As the material is heated the edges of the amorphous mark crystallize and the crystal phase grows towards the center. Simultaneously

crystal nuclei form in the middle of the mark and grow outwards. Nucleation-dominated material crystallization rates are based both on their nucleation and crystal growth rates. They have high nucleation rates. This means that most of the growth in these systems comes from new crystals forming and as such their crystallization rates do not depend strongly on the amorphous mark size. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) is the most commonly used alloy in current device research as well as in optical devices, and is nucleation-dominated.⁷

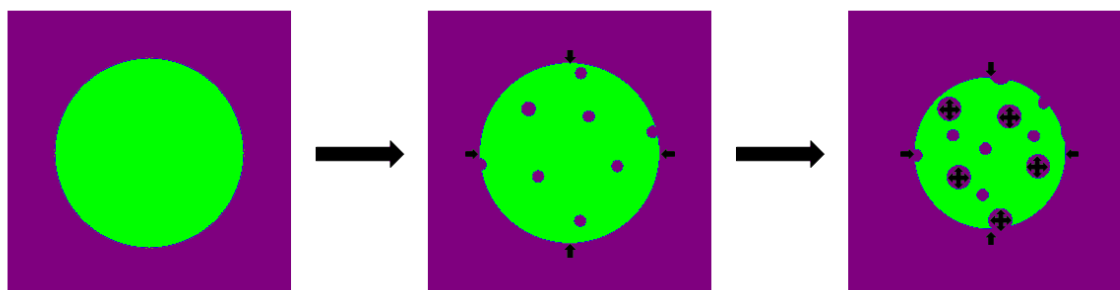


Figure 3: Typical nucleation-dominated crystallization where the light green is the amorphous phase and the dark purple is crystalline material. Crystal growth occurs both from the edges of the mark and from new nucleation events that occur within the amorphous phase.

The other class of PCMs is growth-dominated materials. They are mostly based off high antimony alloys, though germanium telluride (GeTe) is also considered a growth-dominated material. A typical growth-dominated crystallization mechanism is shown in Figure 4. Again the crystalline region grows towards the center of the amorphous mark, however as there is not much nucleation occurring in the material there isn't much crystal growth from within the amorphous region. As there is relatively little nucleation compared to the amount of growth of existing crystal these materials overall crystallization rates are highly dependent on the size of the amorphous mark. This means as the drive for higher data density creates a need for smaller and smaller amorphous spot sizes growth-dominated materials become more advantageous⁷. Many growth-dominated alloys are based on elemental antimony which is characterized by an explosive growth crystallization mechanism.³⁹ This mechanism is caused by an exothermic crystallization reaction that then dumps heat into the surrounding structure thus accelerating the crystallization reaction.¹² The growth-dominated alloy that has been most commonly used in

industry and in research has been silver indium antimonide telluride alloys (AIST) which includes many compositions of material that are based off of Ag- and In- doped Sb_2Te_3 .^{7, 20, 40}

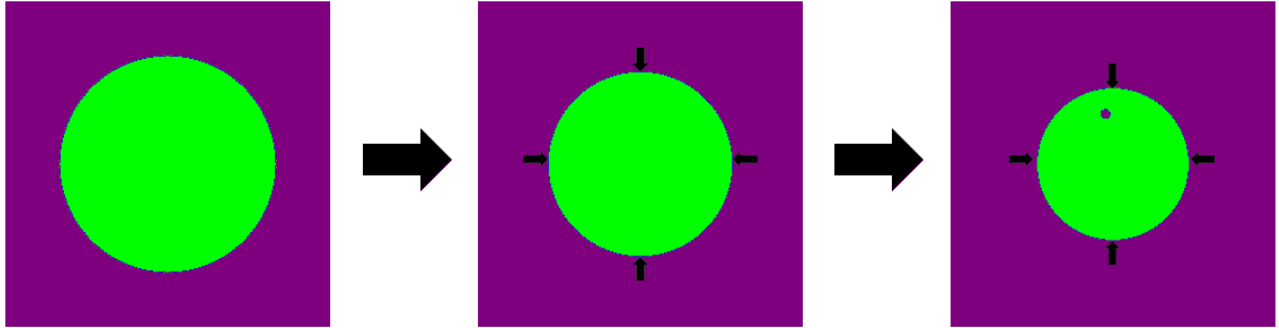


Figure 4: Typical growth-dominated crystallization where the light green is the amorphous phase and the dark purple is the crystalline material. While there are still nucleation events crystallization occurs primarily from the already existing interface between crystalline and amorphous material.

2.2. Nucleation and Growth Kinetics

2.2.1. Nucleation in Amorphous Materials

Nucleation in glassy materials is defined as the formation of small crystallites in the glassy matrix from which the crystalline material will grow. There are two barriers to nucleation: the kinetic barrier, which is the rate at which materials can be moved or rearranged in a material, and the thermodynamic barrier, which is the change in free energy caused when a nucleus is formed. The overall nucleation rate can be described by Equation 1, where I is the nucleation rate, A is a constant that factors in the rate that atoms cross the interfacial boundary and has units of s^{-1} , ΔG^* is the thermodynamic barrier to nucleation, E_{nuc} is the kinetic barrier to nucleation, k_B is the Boltzmann constant, and T is the absolute temperature.

$$I = Ae^{\frac{-(\Delta G^* + E_{\text{nuc}})}{k_B T}} \quad \text{Equation 1}$$

For homogenous nucleation ΔG^* is described by the change in free energy for the formation of a sphere (Equation 2). This equation is derived from the competing effects of interfacial energy

and volumetric free energy in a growing nucleus. For a nucleus below T_m , as its radius increases the volumetric free energy increases by proportional to the volume and the surface energy grows proportionally to the surface area.²¹ For heterogeneous nucleation on a substrate interface, ΔG^* is dependent on the contact angle made between the substrate and the crystallite.

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2} \quad \text{Equation 2}$$

The critical radius for a nucleus to grow, r^* , is related to the change in surface energy, γ , and change in free energy between the final and initial phases per unit mole, ΔG_v , Equation 3.

$$r^* = \frac{-2\gamma}{\Delta G_v} \quad \text{Equation 3}$$

The dependence of E_{nuc} is generally described as a diffusion coefficient, D , using Equation 4, where λ is the atomic jump distance and h is Planck's constant

$$D = \frac{k_B T \lambda^2}{h} e^{\frac{-E_{nuc}}{k_B T}} \quad \text{Equation 4}$$

D can also be related to viscosity, η , using the Stokes-Einstein relation (Equation 5).⁴¹

$$D = \frac{k_B T}{3\pi\lambda\eta} \quad \text{Equation 5}$$

Combining Equation 4 and Equation 5 gives the viscosity dependence of E_{nuc} (Equation 6)⁴¹.

$$e^{\frac{-E_{nuc}}{k_B T}} = \frac{h}{3\pi\lambda^3\eta} \quad \text{Equation 6}$$

The above kinetic equations hold true for strong glasses, glasses that don't readily crystallize, and for fragile glasses, glasses that crystallize easily at higher temperatures, such as PCMs. However, as the temperature approaches T_g , the Stokes-Einstein equation underestimates the diffusion rate for fragile glasses by several orders of magnitude³⁴.

At temperatures around T_x , the nucleation rate can be written as the Arrhenius relationship found in Equation 7. Where I_0 is a pre-exponential constant that represent the nucleation rate at the point where $1/k_B T$ approaches 0.

$$I = I_0 e^{\frac{-E_{nuc}}{k_B T}} \quad \text{Equation 7}$$

For temperatures very close to the melting temperature, ΔG_v is very small which means the size of critical radius is so large that it is very improbable that a nuclei will form. This leads to a range of temperatures below T_m where nuclei will not form. This is called the metastable zone of undercooling. Once past the metastable zone of undercooling the thermodynamic barrier will decrease with decreasing temperature which will cause nucleation rate to increase. After a certain point, the kinetic barrier will become so great that the nucleation rate will begin to drop and eventually drop to a rate of essentially zero.⁴¹

2.2.1.1. Transient Nucleation

In amorphous materials and other metastable solids, there is a phenomenon called transient nucleation. For metastable solids the nucleation rate of a reaction often effectively starts at zero nucleation events per unit time and increases with time up to a steady state nucleation rate that is described by the previous equations. This rate is described by Equation 8, where τ is the relaxation time for the transient nucleation process.⁴²

$$I(t) = I e^{-\tau/t} \quad \text{Equation 8}$$

2.2.2. Growth of Crystal Regions in Amorphous Materials

Like the nucleation rate, growth must overcome a kinetic barrier, E_g . E_g is the activation energy of crystal growth and dictates how fast crystal growth will change with changing temperature.⁴² The general equation for growth rate below T_m is given by Equation 9, where a_0 is the interatomic distance and v is the vibrational frequency of atoms crossing the amorphous-crystalline interface.

$$U = a_0 v e^{\frac{-E_g}{k_B T}} \quad \text{Equation 9}$$

The constants, a_0 and v , can be assume to be a constant for this temperature range and represented by a single constant, U_0 , often referred to as the pre-exponential constant. This pre-exponential constant is the value that U_0 approaches as $1/k_B T$ approaches 0. This simplifies Equation 9 to Equation 10.

$$U = U_0 e^{\frac{-E_g}{k_B T}} \quad \text{Equation 10}$$

Unlike nucleation, there is no metastable zone of undercooling for growth rate and growth will occur at any temperature below the melting temperature.⁴¹

2.2.3. Effect of Substrate and Capping Layer on Nucleation and Growth

Substrate and capping materials selection both can have a large effect on the measured values of kinetic parameters for nucleation and growth. As the interface between the PCM thin film and the substrate or capping layer is a prime location for heterogeneous nucleation the interfacial energy of these interfaces can greatly affect the nucleation rate.²¹ A study by Ghezzi *et al.*⁴³ looked at the differences in nucleation and growth of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe when capped with SiO_2 and when capped with Ta. It was found that when the materials were capped with SiO_2 heterogenous nucleation was preferred at the material interface, but when capped with Ta heterogeneous nucleation was suppressed and homogeneous nucleation became the dominant nucleation mechanism. In addition it was determined that cladding with Ta increased T_x by 12°C and increased E_{comb} from 2.58eV when clad in SiO_2 to 3.48eV when clad in Ta.⁴³

2.2.4. Johnson-Mehl-Avrami-Kolmogorov Analysis

The Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation has been in use since the early 1940's to describe crystallization rates as a function of time. It was developed as a way to be able to calculate crystallization rates when nucleation and growth parameters could not be deconvoluted from each other. The general form of the JMAK equation is given by Equation 11 where $\chi(t)$ is the percentage of volume crystallized at time, t , k is an effective kinetic parameter, and n is the Avrami parameter. The temperature dependence of k can be described using the Arrhenius relationship in Equation 12 where k_0 and E_{comb} are system dependent parameters.^{32, 37,}
⁴⁴ E_{comb} is the activation energy of the entire crystallization process and combines contributions of both nucleation and growth processes.

$$\chi(t) = 1 - e^{-kt^n} \quad \text{Equation 11}$$

$$k = k_0 e^{\frac{-E_{comb}}{k_B T}} \quad \text{Equation 12}$$

Previous studies have written the Avrami parameter as a function of nucleation and growth parameters (Equation 13) where a is the time dependence of the number of nuclei, N , found in Equation 14, b is the dimensionality of growth (1 for needle shaped growth, 2 for discs, and 3 for spheres) and c is dependent of growth type (1 for interface controlled growth and 0.5 for diffusion controlled growth).³²

$$n = a + bc \quad \text{Equation 13}$$

$$N \propto t^a \quad \text{Equation 14}$$

E_{comb} can be approximated as a function of E_{nuc} and E_g using Equation 15.

$$E_{comb} = E_{nuc} + bcE_{growth} \quad \text{Equation 15}$$

k_0 can be approximated as a function of I_0 and U_0 using Equation 16.

$$\ln(k_0) = \ln(I_0) + bc \ln(U_0) \quad \text{Equation 16}$$

Often Equation 11 is rewritten as in Equation 17 so that the slope of the equation is n and the intercept is $n \ln(k)$.⁴⁴

$$\ln \left(\ln \left(\frac{1}{1-\chi(t)} \right) \right) = n \ln(k) + n \ln(t) \quad \text{Equation 17}$$

2.2.4.1. JMAK analysis for thin films

The JMAK equations for bulk can be applied to thin films with a couple of limitations. The Avrami parameter in bulk materials is often assumed to be 4, however for thin films this is not true as this assumption is based on the formation of spherical particles. For a thin film, the ideal Avrami parameter for a time independent nucleation materials and interface controlled growth is 3, if growth is isotropic in the plane of the film (disc shaped). Interface controlled growth means that the limiting rate of crystal growth is the rate at which atoms cross the amorphous-crystalline interface. If the growth is limited by diffusion to the interface then the ideal Avrami parameter would be 2.5.

2.3. Prototypical Phase Change Materials

It is useful to compare the materials systems in this work to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and AIST because they are already in use in commercial products and have well-studied crystallization kinetics.

2.3.1. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225)

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ is the most commonly used and most extensively researched PCM because of its large change in reflectivity upon crystallization (20%)⁴ and ability to easily crystallize. As stated previously it is a $\text{GeTe-Sb}_2\text{Te}_3$ tie line material and is considered a nucleation-dominated material. GST225 has a crystallization temperature around 140°C where it undergoes a transition from amorphous to a metastable distorted rock salt structure and a transition from the distorted rock salt structure to a hexagonal close packed structure around 310°C.²³

In a study by Ruitenber *et al.*³² crystallization kinetics were studied between 140°C and 177°C using in-situ heating in a TEM. Nucleation and growth parameters were calculated individually as well as calculating the combined values using JMAK analysis. These values are displayed in Table I compared with values calculated by Weidenhof *et al.*²⁵ and Jeong *et al.*²⁶ which were measured using reflectivity. Jeong *et al.* noted a two-part crystallization where there is a higher activation energy first stage followed by a lower activation energy second stage. It was theorized by both Ruitenber *et al.* and Jeong *et al.* that this two stage crystallization is due to the material being fairly thick (200nm) and therefore causing a nucleation stage where nucleation occurs at the interface between the material and the substrate or capping layer, followed by a second stage where the grains impinge and grow in a plate-like front.

Table I: JMAK parameters for GST225

	Ruitenber <i>et al.</i> ³²	Weidenhof <i>et al.</i> ²⁵	Jeong <i>et al.</i> ²⁶ 1 st stage	Jeong <i>et al.</i> ²⁶ 2 nd stage
N	4.3 ± 0.9	2.6 ± 0.1	3.56-5.75	1.03-1.25
$\ln(k_0)$	53 ± 12	51	-	-
E_{comb} (eV)	1.8 ± 0.5	2.0 ± 0.2	2.26	1.98

Orava *et al.*³⁴ used ultra-fast DSC to look at crystallization characteristics in the temperature range above T_g but below T_{max} (177°C-377°C). Orava *et al.* looked at whether the crystallization in this temperature range is dependent on viscosity like those at higher temperatures or whether it can be decoupled from viscosity and is an Arrhenius relationship like rates around T_g . It was shown that the Arrhenius relationship exhibited at low temperatures is not valid as

temperature increase and that GST225 is a very fragile glass ($m=90$) which indicates that crystallization is extremely temperature dependent and will crystallize rapidly at high temperatures. It was also determined that the maximum growth rate was around 2.9 m/s and occurred at $0.76T_m$ or 410°C as can be seen in Figure 5. The study assumed that the activation energy found in Kissinger analysis is the activation energy of crystal growth even though GST225 is a nucleation-dominated material.³⁴ This was backed up by research done by Kelton, but it was stipulated that there is a large gap between the nucleation and growth temperature regimes.⁴⁴ Orava justified their assumption by citing calculations done by Russo *et al.*⁴⁵ that said that in the temperature range at which the ultra-fast DSC were conducted the nucleation rate is decreasing with increasing temperature (Figure 6).

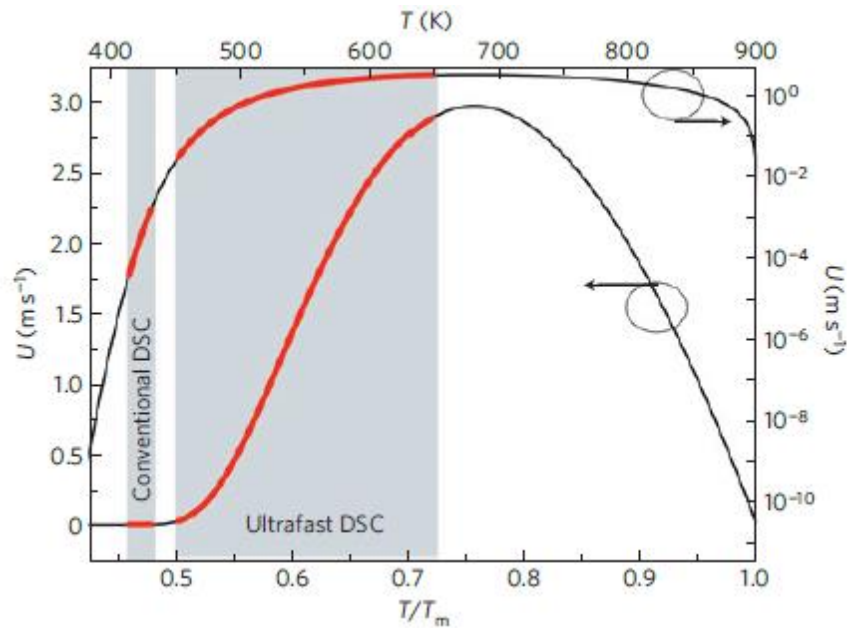


Figure 5: Growth Rate of GST225 Calculated Using DSC. Conventional DSC is used around the glass transition temperature while ultrafast DSC is utilized from 50% of the melting temperature up to T_{max} .³⁴

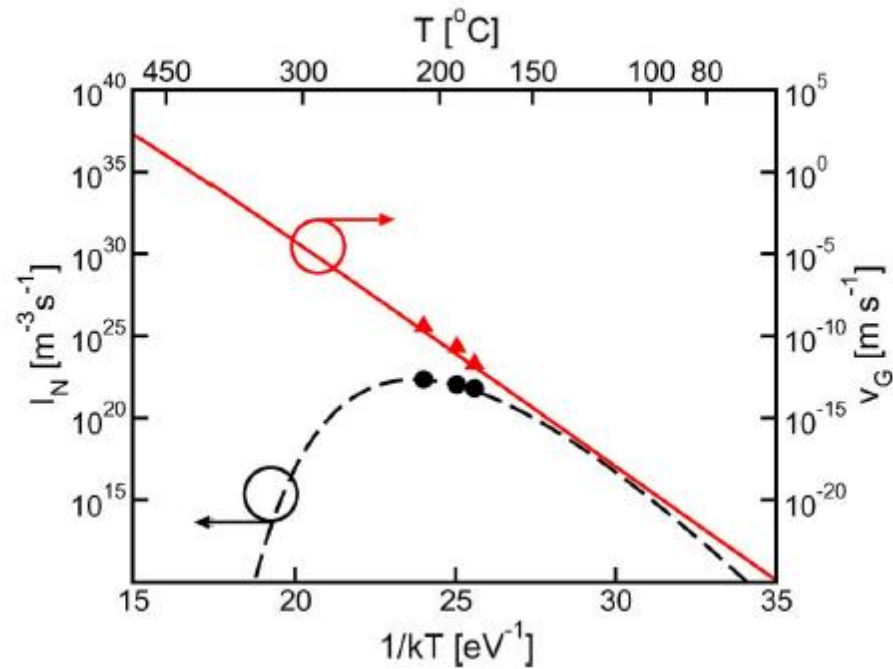


Figure 6: Nucleation (black dashed line) and crystal growth (red line) rates of GST225. As can be seen the nucleation rate starts to decrease with increasing temperature above 180°C.⁴⁵

2.3.2. AIST

AIST is the most commonly used growth-dominated phase change material. The exact composition of the material varies however most AIST compositions are based off Sb_2Te with small amounts (<10 at. %) of silver and indium as dopants. AIST has a hexagonal structure similar to that shown in Figure 7 but with layers of silver and indium atoms substitutionally incorporated.⁴⁰

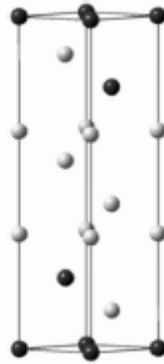


Figure 7: Crystal structure of Sb_2Te . The black atoms are Sb and the white are Te.⁴⁰

The crystallization temperature of AIST varies with exact composition, film thickness, and capping layer but is generally between 150°C-175°C.¹³

Salanga *et al.*¹⁴ used laser reflectivity measurements to measure the growth velocity of AIST from 100 nm/s at 145°C up to >3m/s at 280°C. The entire region exhibited a strictly Arrhenius relationship with an activation energy of 2.7 eV. From these growth rates viscosities were determined. Kalb *et al.*¹⁵ used AFM to measure the growth velocities for a temperature range of 140°C-185°C. A value of 3.025×10^{24} m/s was calculated for U_0 and an activation energy of 2.90 eV was found.

2.4. Materials Systems Used in This Work

2.4.1. GeTe

2.4.1.1. Phase Diagram

Figure 8 shows the Ge-Te phase diagram. As can be seen at room temperature up to about 375°C there are three phases present: germanium, tellurium and GeTe.⁴⁶ In addition there is a eutectic at 85 at% Te at 375°C.

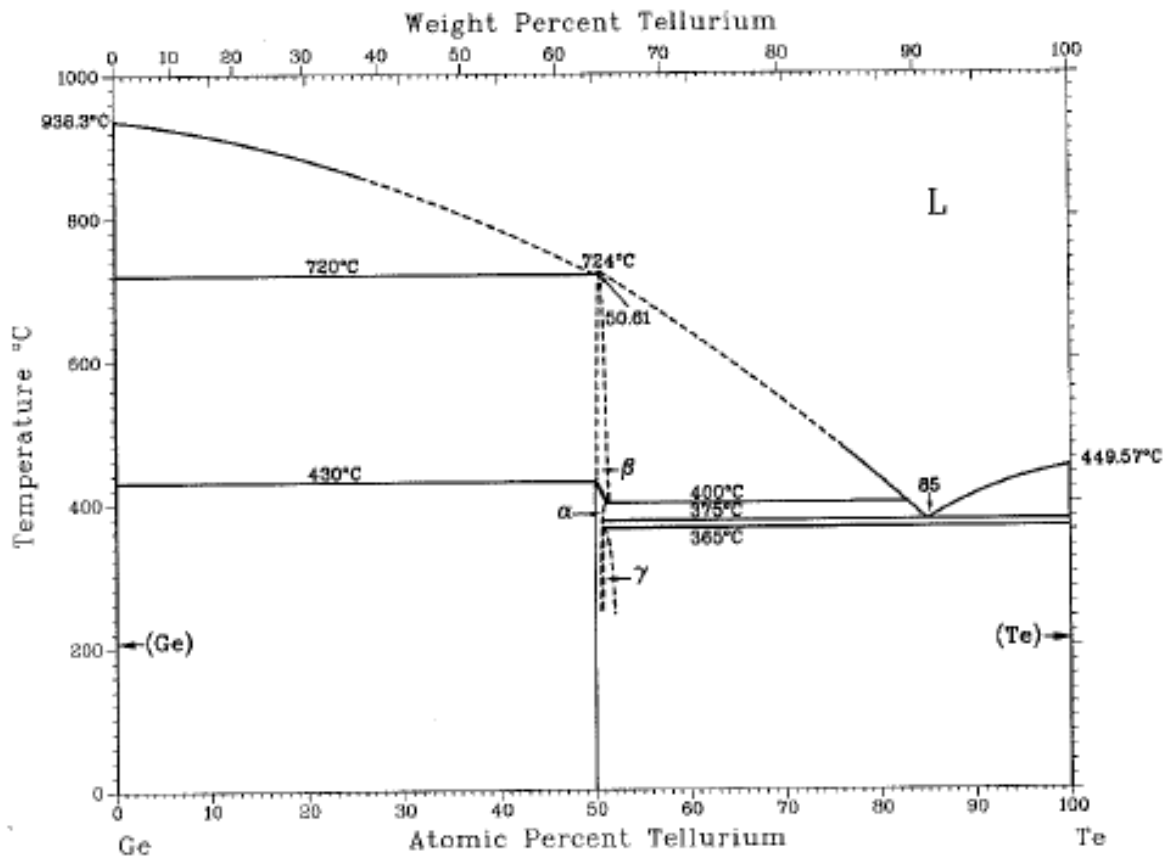


Figure 8: Ge-Te phase diagram⁴⁶

Figure 9 is a magnified view of the GeTe part of the phase diagram. As can be seen the phase has a slight solubility for excess tellurium. GeTe has two polymorphs: α -GeTe at low temperatures and β -GeTe and melts congruently at 724°C.⁴⁶

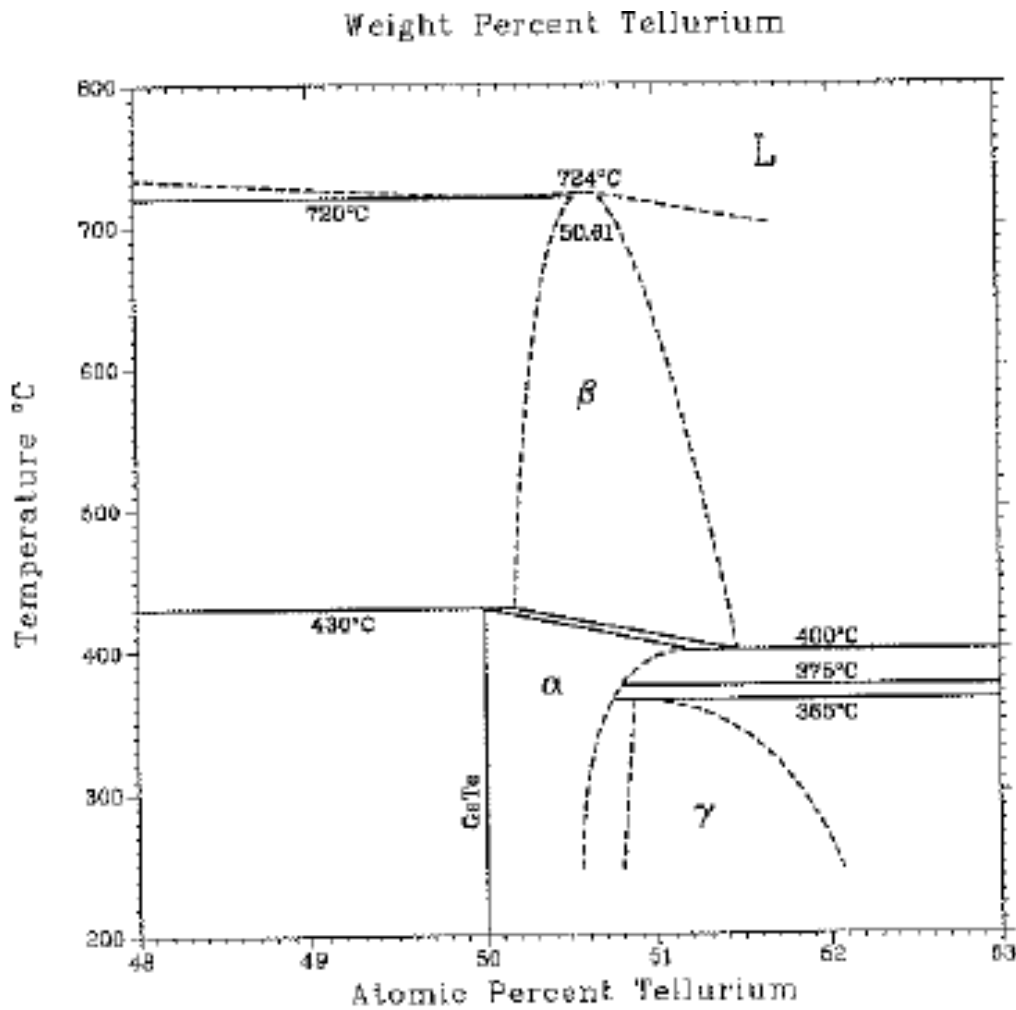


Figure 9: Magnified View of the GeTe Phase²⁷

2.4.1.2. Literature Review

GeTe is by far the most studied system examined in this work due to its simplicity and being one of the two constituent structures of the Sb_2Te_3 -GeTe pseudo-binary tie line. There has been characterization of crystal growth rates across the entire temperature spectrum,^{27, 29-31, 33, 36-37} however the substrate material and capping material has not been consistent along the entire spectrum. The low temperature crystallization kinetics have been measured by TEM, optical reflectivity measurements and optical microscopy in several studies.^{24, 26-28, 31} These values are summarized in Table II.

Table II: Low temperature crystallization measurements of GeTe

	Bastard <i>et al.</i> ³³	Libera <i>et al.</i> ²⁷	Lu <i>et al.</i> ²⁹	Mio <i>et al.</i> ³⁰	Salinga <i>et al.</i> ³¹
Temperature Range	120°C-155°C	167°C-185°C	140°C-152°C	143°C-155°C	160°C-180°C
Technique	in-situ TEM	in-situ optical reflectivity	in-situ transmission optical microscopy	in-situ reflection optical microscopy	ex-situ reflection optical microscopy
Substrate	Insulator-removed by ion milling	Borosilicate Glass	Glass	SiO ₂ on Si	Si
Capping Layer	Insulator-removed by ion milling	None	none	none	none
E_g	1.45eV	-	1.77eV	2.0eV	2.27eV
U_0	-	-	5.9×10^{14} m/s	7.0×10^{14}	-
E_{nuc}	-	-	-	4.3eV	-
I_0	-	-	-	$5.4/\text{m}^2\text{s}$	-
E_{comb}	-	1.7eV	1.7eV	-	-
n	-	4.5	4.0	-	-

Mio *et al.*³⁰ looked at the effect of ion irradiation of the sample prior to annealing. It was determined that irradiation caused a faster crystallization likely due to the relaxation of the amorphous structure to one more like the crystalline structure. Chen *et al.*³⁶ looked at the crystallization kinetics of GeTe from 217°C to 287°C using ultrafast DSC. This study made all the assumptions about crystal growth rate as mentioned above in Orava *et al.*³⁴ Using the data resulting from the ultrafast DSC experiments and in-situ sheet resistance measurements at lower temperature to evaluate the fitness of the Mauro, Yue, Ellsion, Gupta, and Allan (MYEGA) and Cohen and Grest models, two models that relate growth rate to viscosity. It was determined that the MYEGA model fit the data well. The MYEGA model was then used to calculate that the

maximum growth rate is 3.5m/s and occurred at 517°C (0.79 of T_m). Santala *et al.*³⁷ used DTEM to look at the growth rates around T_{max} . The study used a simulated temperature profile to estimate temperature of the sample as a function of distance from the center of laser. It was concluded that the temperature range that was being measured on was higher than that of T_{max} since the growth rate decreases as a function of time which would indicate that as heat is released due to crystallization the rate decreases. The maximum growth rate measured in this experiment was approximately 3.8 m/s which indicates a good agreement with the calculation of U_{max} in Chen *et al.*

2.4.2. GeSb₆Te (GST161)

2.4.2.1. Phase Diagram

Figure 10 shows the Ge-Sb-Te ternary phase diagram with the composition of Ge₁Sb₆Te₁ (GST161) marked with a red x. GST161 has a melting point of between 550°C and 600°C.⁴⁷

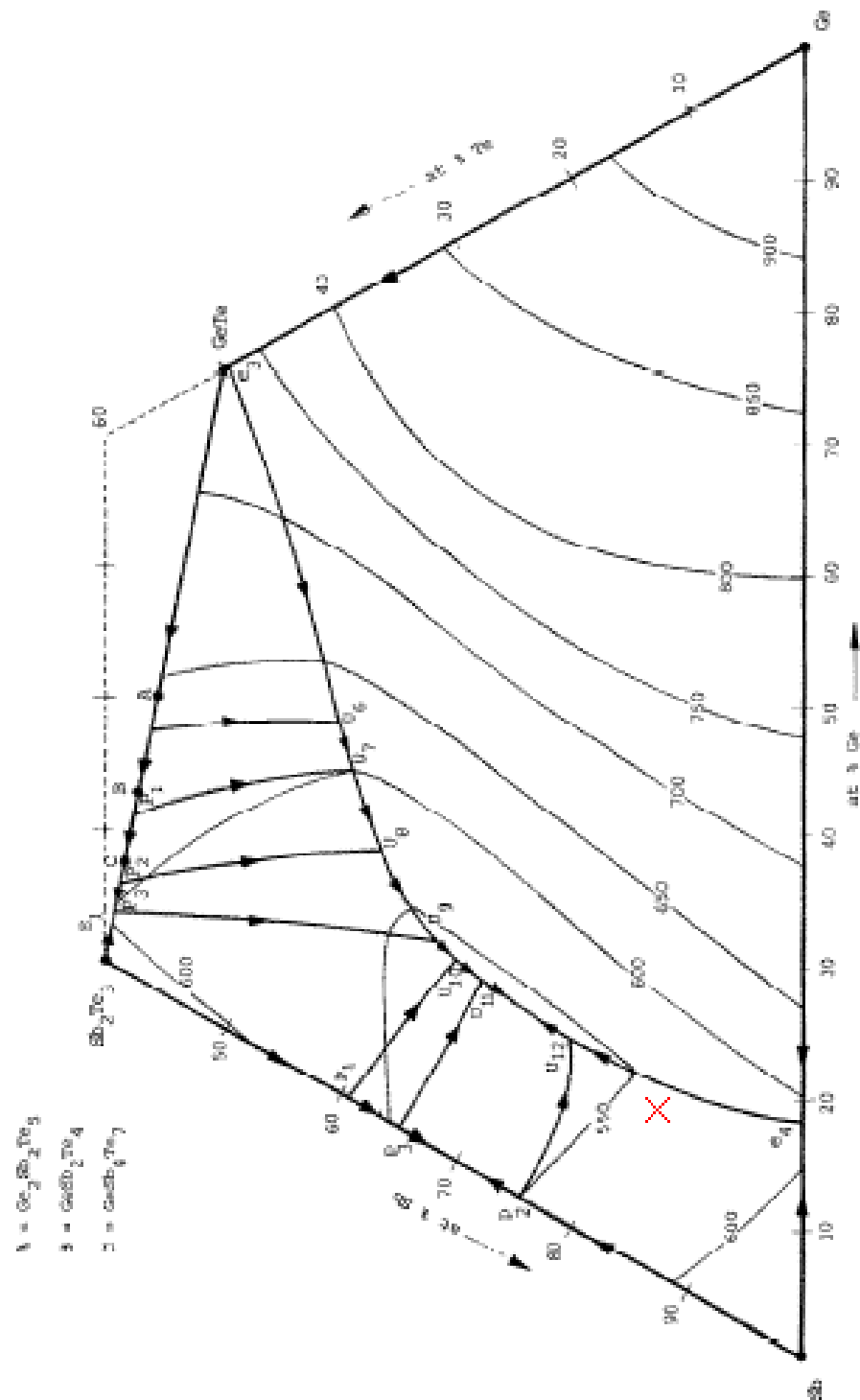


Figure 10: Ge-Sb₂Te₃-GeTe phase diagram. The red x indicated the composition of Ge₁Sb₆Te₁.⁴⁷

Figure 11 shows a vertical section of the phase diagram with 10 at% Ge content. The composition of $\text{Ge}_{10}\text{Sb}_{77.5}\text{Te}_{12.5}$ is highlighted and is similar to the composition of GST161 with 2.5 at% excess of Sb and 2.5 at% deficient of Ge. There is a eutectic near this composition where Sb and liquid converts to Sb plus Ge and δ phases upon cooling below 529°C.

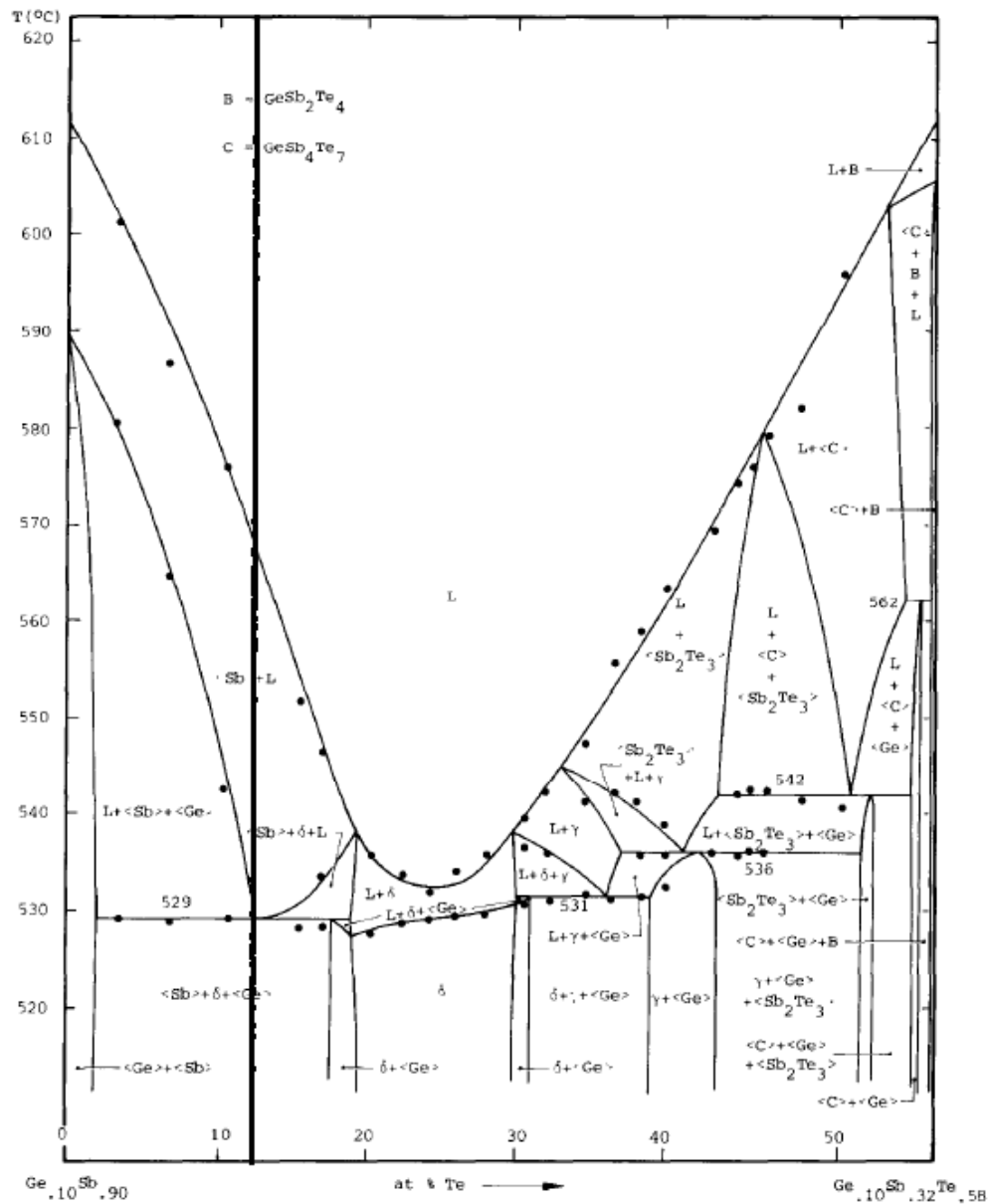


Figure 11: Vertical section of ternary phase diagram with a constant 10% Ge content⁴⁷

2.4.2.2. Literature Review

Unlike GeTe there has been relatively little research into GST161 but there is an interest in it as a potential PCM due to its high growth rate. Cheng *et al.*⁴⁸ examined compositions along the GeTe-Sb pseudo-binary for optical reflectance properties and crystallization temperature found using in-situ X-ray diffraction. Figure 12 shows the dependence of crystallization temperature on antimony content. The crystallization temperature reached a maximum at a composition of $\text{Ge}_1\text{Sb}_1\text{Te}_1$ of 278°C and GST161 has a crystallization temperature of 240°C. GST161 crystallized into a rhombohedral structure that was similar to that of elemental antimony and had either a second phase transition or texture change at 445°C. As can be seen in Figure 12 the recrystallization time of GeTe-Sb materials is maximized at low antimony and high antimony alloys. The maximum change in contrast of GST161 is around 5%, much lower than the 20% found in GeTe. Overall, the study concluded that GST161 and other high antimony GST alloys could be suitable candidates for phase change memory due to its high crystallization temperature and fast recrystallization times.

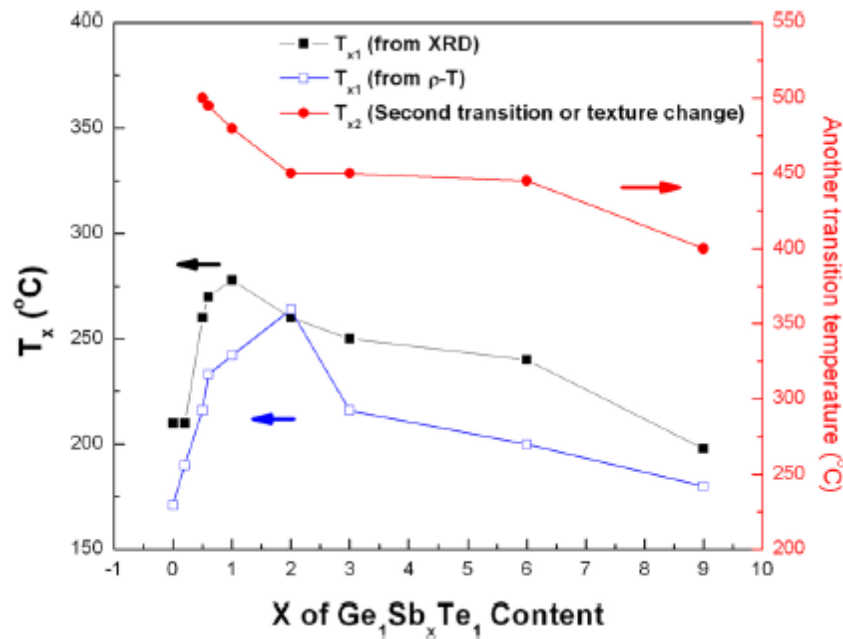


Figure 12: Crystallization temperature of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ⁴⁸

Winseck *et al.*³⁸ used DTEM to look at the crystal growth rate near T_{max} . A laser was used to heat the sample and nine images were taken over 4 μs . For as-deposited films, a maximum crystal

growth rate of 10.8 m/s was found. Experiments were also run on pre-annealed sample but the crystal growth front passed out of the field of view by the second frame, but which indicated a crystal growth rate that exceeded 17.8 m/s, which is far faster than any previously reported growth rate value for a PCM alloy. In addition, it was noted that growth rates dropped off as the growth front propagated into cooler parts of the sample and that this drop-off was accompanied by a change in microstructure from large grains to small columnar grains. This suggests that a change in growth mechanism may occur. Two theories were put forth. The first theory is that the growth goes from the crystallization of an undercooled liquid at the center of the laser mark to growth from an amorphous solid. The second theory is the change from growth of an undercooled liquid to liquid-phase mediated growth similar to the explosive crystallization found in elemental Sb. The growth rate difference may also be explained by the fact that the laser had a Gaussian energy distribution which would cause a temperature gradient across the window.

While there has been little research on the specific composition of GST161, there has been some research into high antimony Ge-Sb alloys. Raoux *et al.*⁴⁹ measured the crystallization temperature, electrical contrast, and optical contrast for Ge-Sb films with germanium contents between 7.7 at. % and 81.1 at. %. It was found that as germanium content increased the crystallization temperature increased as well. Both optical and electrical contrast were maximized at the eutectic point that occurs at 85 at.% germanium with values of 30% optical contrast and around three orders of magnitude difference in electrical contrast.

Eising *et al.*⁵⁰ looked at the crystallization of Ge-Sb alloys with compositions between $\text{Ge}_6\text{Sb}_{94}$ and $\text{Ge}_{10}\text{Sb}_{90}$. It was determined that as germanium content increased T_x increased from 80°C for $\text{Ge}_6\text{Sb}_{94}$ to 200°C for $\text{Ge}_{10}\text{Sb}_{90}$. The activation energy of crystal growth increased as well, from 1.7eV to 5.5eV. It was also found that for compositions that had greater than 8 atomic% germanium there were two competing modes of growth; one slow growth mode which created circular grains with smooth edges and a second faster growth mode that created triangular grains with rough edges. The slow growth mode is more dominant at lower temperatures while the fast mode is dominant at higher. Using AFM and EDS it was determined that the two different modes had the same chemical composition but that the faster growth mode had a dendritic growth structure and a larger change in height upon crystallization. It was theorized

that the slow growth mode was caused by the crystallization of a homogenously alloyed crystal while the fast mode was accompanied by a partial phase separation of the material which released large amounts of latent heat into the material.

Van Pieterse *et al.*²⁰ looked at the crystallization temperature, crystallization activation energies, and time it took to erase amorphous marks of 125 nm radius on several compositions of material based on Sb or SbTe. From these times they extrapolated an archival life for the material assuming operating temperatures of 50°C. These results are shown in Table III. They concluded that, in general, adding dopants like germanium slowed the crystallization rate but greatly increased the stability of the amorphous phase and additions like tin and indium do the opposite.

Table III: Kinetics values for high antimony Ge-Sb alloys²⁰

	Ge ₈ Sb ₇₂ Te ₂₀	Ge ₁₂ Sb ₈₈	Ge ₁₅ Sb ₈₅	Ge ₂₂ Sb ₇₈
T _x (°C)	222	-	250	271
E _{comb} (kJ/mol)	-	-	237	346
t _{xtallization} (ns)	33	13	15	23
Archival life (@50°C) (years)	-	-	1*10 ⁶	3*10 ¹⁴

2.4.3. Ga₁₅Sb₈₅

2.4.3.1. Phase Diagram

Figure 13 shows the Ga-Sb phase diagram. There are 3 solid phases present: the gallium phase, the antimony phase, and GaSb phase. In addition there is a eutectic at about 88.2 at% gallium with a transformation temperature of 589.3°C.⁵¹

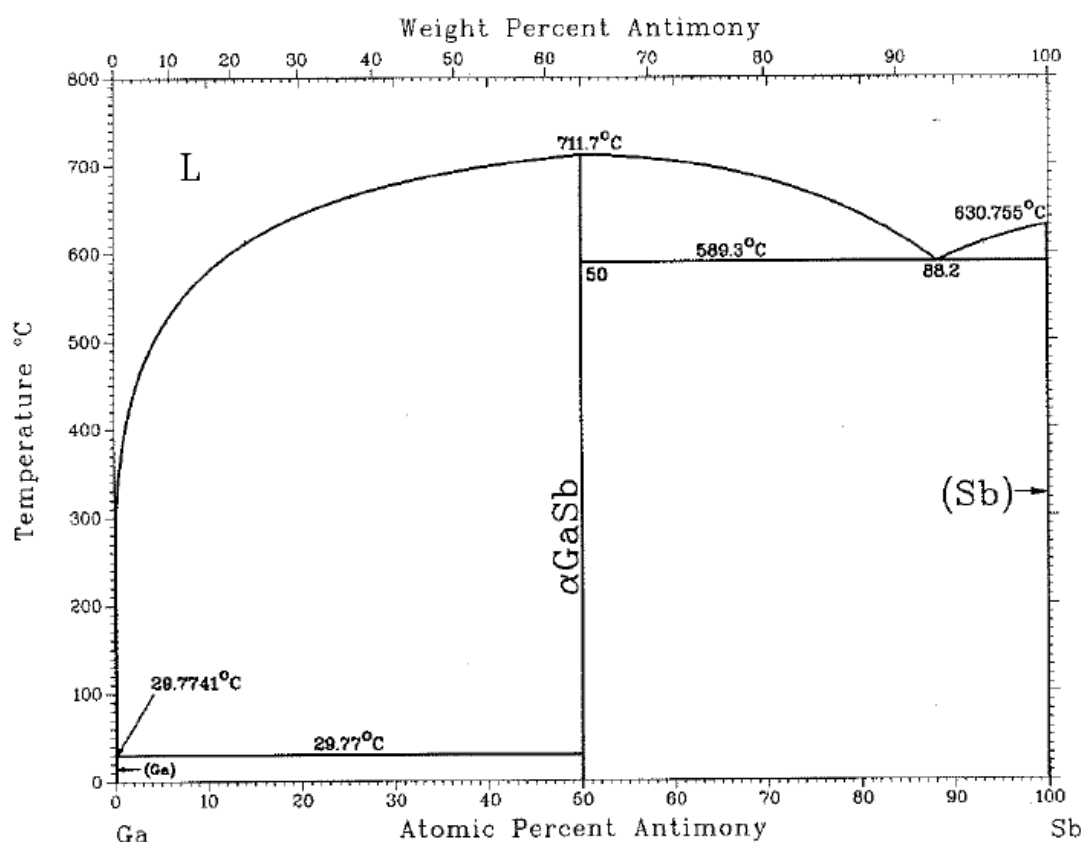


Figure 13: Ga-Sb phase diagram⁴⁶

2.4.3.2. Literature Review

Ga₁₅Sb₈₅ has also had relatively little research published on its crystallization properties. Raoux *et al.*¹⁷ looked at the crystallization temperature, change in resistivity, and change in reflectance of Ga-Sb with compositions ranging from Ga₄₆Sb₅₄ to Ga₁₃Sb₈₇. It was found that there are two crystallization temperatures, one for the stoichiometric GaSb phase that decreases with increasing antimony content and one for the Sb phase which decreases with increasing antimony content and that these temperatures are roughly equal at the composition Ga₂₇Sb₇₃. The composition closest to Ga₁₅Sb₈₅, Ga₁₃Sb₈₇, had crystallization temperatures of 187°C for the Sb phase and ~355°C for the GaSb phase. Change in reflectivity are initially negative for compositions around the GaSb phase composition, but become more positive as antimony content increase and reach a maximum magnitude change at the Ga₁₃Sb₈₇ composition with a

20% change in reflectance. The change in resistivity has a maximum of 5 orders of magnitude at $\text{Ga}_{36}\text{Sb}_{64}$ with the $\text{Ga}_{13}\text{Sb}_{87}$ having a change of 2 orders of magnitude.

A second study by Raoux *et al.*¹⁶ for compositions between GaSb and $\text{Ga}_8\text{Sb}_{92}$ found crystallization temperatures, crystallization time and reflectance data. Unlike the first study the samples were melt-quenched as opposed to as deposited. The reflectivity data found similar results as the previous study with $\text{Ga}_{14}\text{Sb}_{86}$ having a maximum magnitude of 20% change in reflectivity however increasing antimony beyond this composition resulted in decreasing contrast. A big difference between the two studies is that the crystallization temperature for the GaSb phase and the Sb phase cross at a higher antimony content with it crossing at $\text{Ga}_{14}\text{Sb}_{86}$ with a temperature of $\sim 225^\circ\text{C}$. The crystallization time of the eutectic composition is much higher than any other composition as can be seen in Figure 14.

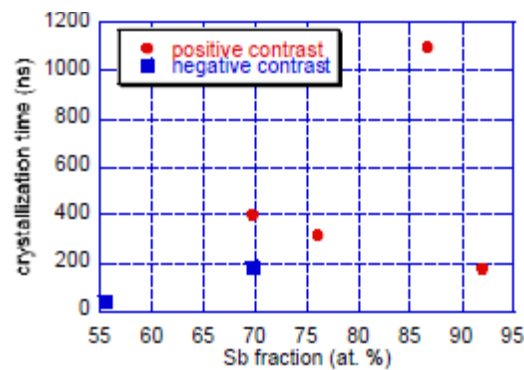


Figure 14: Crystallization time of amorphous Ga-Sb alloys as a function of amount antimony¹⁶

Chang *et al.*¹⁸ used resistance measurements to calculate the crystallization activation energy and pre-exponential factor (k_0), kinetic exponent and the temperature at which the material has a ten year data retention life for compositions of Ga-Sb varying from 77% antimony to 91% antimony. It was determined that both the activation energy and k_0 had maximum values at a composition of $\text{Ga}_{19}\text{Sb}_{81}$ of 8.3eV and $4.7 \cdot 10^{82} \text{ min}^{-1}$ respectively. The composition closest to $\text{Ga}_{15}\text{Sb}_{85}$, $\text{Ga}_{16}\text{Sb}_{84}$, had values of activation energy and k_0 corresponding to 6.9eV and $1.6 \cdot 10^{70} \text{ min}^{-1}$ however there is a larger decrease in activation energy to 3.3eV and a large decrease in k_0 to $3.1 \cdot 10^{35} \text{ min}^{-1}$ with a change in composition to $\text{Ga}_{13}\text{Sb}_{87}$. For $\text{Ga}_{19}\text{Sb}_{81}$ it was determined by comparing the kinetic exponents across temperatures that below 240°C crystallization can be characterized as a combination of new nuclei forming and growth from existing nuclei whereas

above 240°C crystallization occurred solely due to crystallization from existing nuclei. The ten year data retention temperature for Ga₁₉Sb₈₁ was found to be 180°C, significantly higher than that of Ge₂Sb₂Te₅ which has a temperature of 86°C.

Van Pieterse *et al.*²⁰ looked at the crystallization temperature, crystallization activation energy, and time it took to crystallize an amorphous, $t_{\text{xtallization}}$, mark of several Sb and SbTe based alloys including Ga₁₅Sb₈₅. From these times they extrapolated an archival life for the material assuming an operating temperature of 50°C. These values are shown in Table IV.

Table IV: Kinetics parameters values for Ga₁₅Sb₈₅²⁰

	Ga ₁₅ Sb ₈₅
T_x (°C)	233
E_{comb} (eV)	3.34
$t_{\text{xtallization}}$ (ns)	31
Archival life (@50°C) (years)	3×10^{10}

3. Materials and Methods

3.1. Materials

Ge₁Sb₆Te₁ and GeTe thin films of 30nm thickness were sputter-deposited onto Norcada 3mm Si substrate discs with a 10nm SiN_x^a surface film and 9 etched windows at IBM in Yorktown Heights, NY. Ga₁₅Sb₈₅ was also sputter-deposited to a thickness of 30nm with a 7nm SiO₂ capping layer sputtered over onto the same type substrates at IBM.

3.2. Initial experiments

Initial in-situ crystallization tests were done for each material on a Linkam LTS 420 hot stage^b starting at 20°C below the reported crystallization temperature and temperatures and frame times were adjusted accordingly until a range of temperatures were found for each material that would allow for at least 6 images of crystal growth at a minimum of 5 minute intervals could occur using optical microscopy. During these initial experiments, it was found that

^a Part # TA301Z, Norcada, Edmonton, Alberta, Canada

^b LTS 420, Linkam Scientific, Epsom, England, UK

crystallization was slowing down and stopping before completion. This was theorized to be due to oxidation and a nitrogen purge was added to the hot stage system and the $\text{Ga}_{15}\text{Sb}_{85}$ was capped. Light sensitivity was also noticed in the $\text{Ge}_1\text{Sb}_6\text{Te}_1$ and steps were taken to minimize light exposure during GST161 runs.

3.3. GeTe

Capped GeTe was successfully grown ex-situ on a Corning hotplate during initial experiments, however the surface temperature of the hot plate was not consistent enough to determine an accurate temperature. When new samples of GeTe were produced they were unable to be capped as the sputter system that was used to make the samples did not have a SiO_2 or Al_2O_3 target. When these samples were tested the crystallization would slow and stop as was previously seen with other uncapped materials. Unfortunately, the samples also oxidized in ambient conditions as with each successive test the time till arrested crystallization got shorter. By the time the nitrogen purge system arrived the GeTe samples did not crystallize at all. Due to these reasons, accurate crystallization data was not successfully collected for GeTe.

3.4. In-situ optical microscopy of $\text{Ge}_1\text{Sb}_6\text{Te}_1$.

For each temperature, a single specimen was placed on a borosilicate glass microscope slide in a Linkam LTS 420 hot stage with a nitrogen purge to ensure that oxidation of the sample did not occur. Before heating, nitrogen was flowed through the sample chamber at the maximum rate allowed by the flow meter, approximately 0.3L/min, for at least ten minutes. The nitrogen flow was then reduced to approximately 30mL/min and the hot stage was brought up to temperature at a heating rate of 50°C/min. Images were taken at 50X magnification on a LEICA DM 2700M optical microscope operating in reflectance mode of a region on the specimen that was free of windows, scratches, and other defects once the hot stage reached temperature. If a bubble in the film appeared after the initial image, a new location was found that was clear. The temperature was held to within a tolerance of $\pm 0.1^\circ\text{C}$ for the duration of the run. The microscope was then turned off until a time approximately 10-15 minutes before evidence of first crystallization of the next highest temperature experiment. From that point until first nucleation, the microscope was turned on every five minutes to take an image and then subsequently turned off again to minimize growth enhancement due to illumination. Once nucleation occurred the microscope was turned on and images were taken at a fixed time interval that depended on temperature shown in Table V. Each run was considered complete

when the entire frame of view was completely crystallized apart from some small seams between growth fronts. The hot stage was then turned off and allowed to cool to room temperature. A 5x magnification image was then taken to ensure that crystallization occurred homogenously and there wasn't an area of accelerated growth in the region where the microscope was focused.

Table V: Imaging times for GST161

Temperature	Time between images	First image time
185°C	15 min	60 min
187.5°C	10 min	50 min
190°C	5 min	15 min
192.5°C	5 min	15 min
195°C	5 min	5 min

3.4.1. Acceleration of growth due to light exposure

A run was performed on a $\text{Ge}_1\text{Sb}_6\text{Te}_1$ specimen at 195°C using the above procedure except that the microscope was turned on for the entire run. The time between images for this specimen was 5 minutes.

3.5. In-situ optical microscopy of $\text{Ga}_{15}\text{Sb}_{85}$

A $\text{Ga}_{15}\text{Sb}_{85}$ specimen was placed on a borosilicate glass slide inside the Linkam LTS 420 hot stage and nitrogen was flowed through at a rate of about 0.3L/m for at least 10 minutes. The nitrogen flow rate was then reduced to 30mL/min and the hot stage was brought up to temperature at a ramp rate of 50°C/min and an image was taken at 50x magnification. Temperature was controlled to a tolerance of $\pm 0.1^\circ\text{C}$. Images taken for $\text{Ga}_{15}\text{Sb}_{85}$ runs were done in black and white and with an elevated gamma value of 2.51 to enhance the poor contrast seen between the amorphous and crystalline regions. Images were taken at regular frame intervals that depended on temperature as shown in Table VI. The runs were considered done when only small seams between growth fronts were uncrystallized. Once this occurred the hot stage was turned off and the sample was allowed to cool to room temperature. Unlike in the $\text{Ge}_1\text{Sb}_6\text{Te}_1$ runs the microscope was not turned off between images because the samples did not show a significant

increase in degree of crystallinity where the microscope was focused and leaving the microscope on allowed for observation of the sample during the run.

Table VI: Time between images for $Ga_{15}Sb_{85}$

Temperature	Time between images
170°C	30 min
172.5°C	20 min
175°C	20 min
177.5°C	5 min
180°C	5 min

3.6. Image processing

Both $Ge_1Sb_6Te_1$ and $Ga_{15}Sb_{85}$ images were subjected to the same image processing operations. All image processing was done in ImageJ^c. The first operation performed was background correction to eliminate illumination effects. The image take at 0 minutes for each run was subtracted from each image in the run to produce a background subtracted image. These images were then converted to 16-bit binary images. These images were the ones used in the measurement of crystal growth rate. The images were manually thresholded by picking several crystal features in the images and thresholding until only the crystalline regions were black. The despeckle operation was then used to remove random noise and erode and dilate functions were used to smooth out the edges of the grains. These images were used in the JMAK analysis.

3.7. Grain size measurement

Grain size measurements were performed on the 16-bit black and white images with between 15 and 25 grains measured for each run. Each grain had to have at least 3 frames where it had a clearly defined shape but had not impinged with another grain. To measure grain size an ellipse was manually fitted to the grain and the area of the ellipse was measured using ImageJ. Grain

^c ImageJ v1.48, National Institute of Health, USA; Plugins: Calculator Plus

radius was calculated for a circle of the same area as the grain measured. Velocity was calculated both between each frame and by performing a linear regression.

3.8. JMAK analysis

Images were cropped such that any artefacts, such as excess reflection from a nearby window, and inconsistencies such as large scratches or sites that enhanced nucleation were not included in analysis. ImageJ was used to measure the percent of the area of the thresholded images that was black, which indicated the area was crystallized. For the $\text{Ge}_1\text{Sb}_6\text{Te}_1$ the JMAK analysis was done with an incubation time included. The incubation time was calculated by taking the average radius of the grains measured in the earliest frame of each grain size measurement set and using average velocity to back calculate the time at which the average grain size would be zero.

4. Results

4.1. $\text{Ge}_1\text{Sb}_6\text{Te}_1$

4.1.1. Image Collection

Images were taken at 50x magnification and at regular intervals with frame times and temperatures as listed in the materials and methods. Figure 15 shows the run that was performed at 190°C. All GST161 runs were done with illumination minimized. There is a significant delay before signs of nucleation appear with the first evidence of nucleation appearing around the 30 minute mark. Around the 30 minute mark a large number of grains appear and grow very rapidly. The large delay before first nucleation followed by a large number of nucleation events is characteristic of a material that has an incubation time for nucleation. Though it is difficult to determine by just looking at there appears to be little to no nucleation occurring beyond the mass nucleation event. These nucleation characteristics are seen consistently among all $\text{Ge}_1\text{Sb}_6\text{Te}_1$ runs.

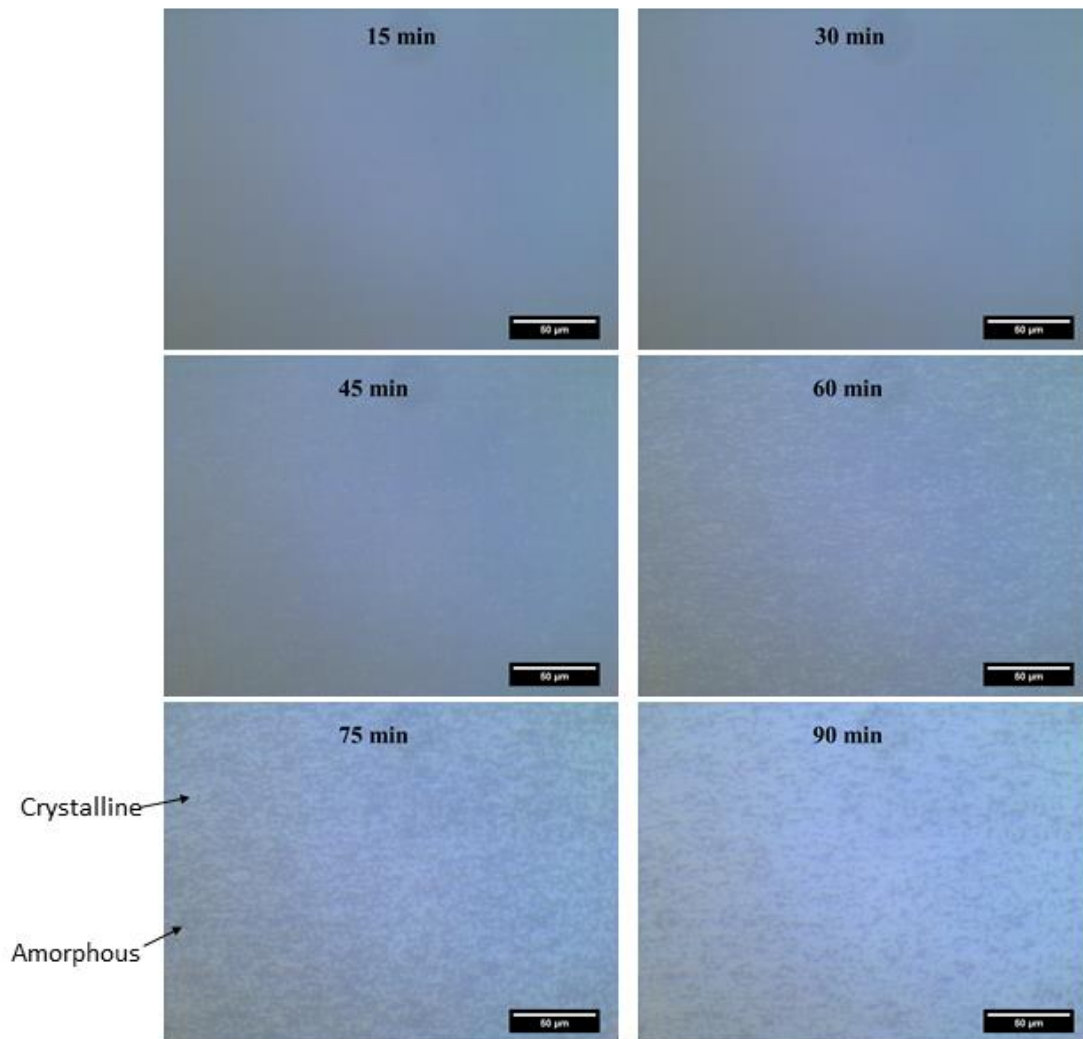


Figure 15: Raw images of $\text{Ge}_1\text{Sb}_6\text{Te}_1$ 190°C run. Nucleation appears to be delayed with a large number of nuclei appearing all at once.

4.1.2. Growth analysis

Growth measurements were done on background subtracted 16-bit black and white images where the grains had distinct shape and hadn't impinged with other grains. Figure 16 shows the set of images used to measure growth data for 190°C and represents a typical set of images.

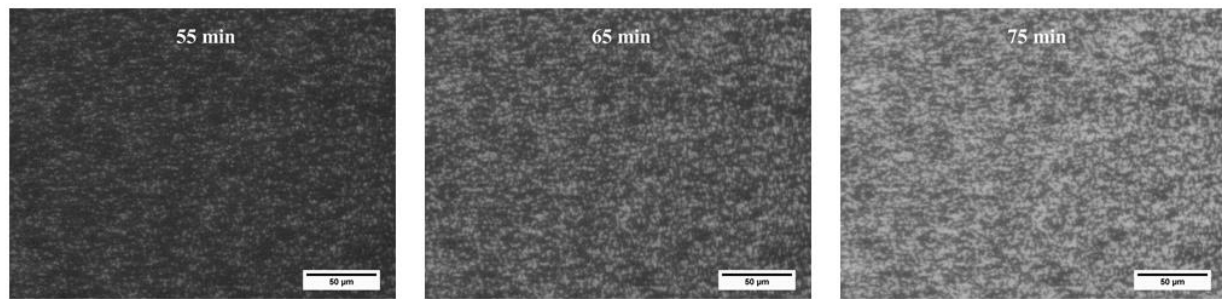


Figure 16: Background subtracted measurements used to measure grain size for the 190C $\text{Ge}_1\text{Sb}_6\text{Te}_1$ run.

This set of images represents a typical set used.

Individual growth measurements are shown in Figure 17. The estimated error in measurement of grain size is $\pm 10\%$ of the radius. The individual measurements appear to have a lot of variation in slope, however when taken as a whole, there appears to be a consistent slope. It should be noted that, for the most part, the initial grain size appears to be similar amongst all grains. These grain measurements were then used to create velocities by both measuring the slope between each individual measurement and by doing a linear regression for each grain.

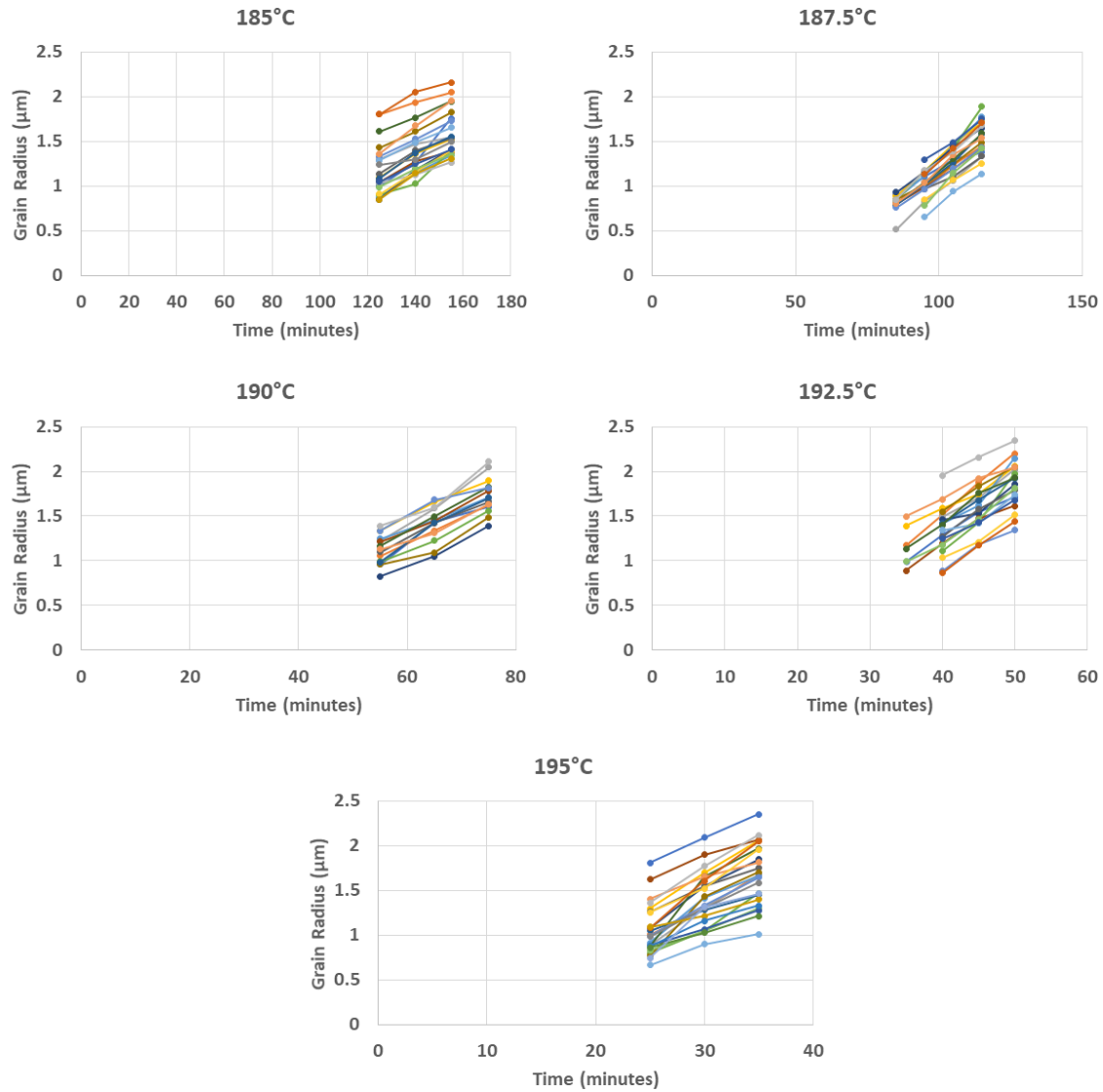


Figure 17: Grain size measurements for $\text{Ge}_1\text{Sb}_6\text{Te}_1$. Grains do not have a constant slope but when taken together a clear slope is apparent. The estimated error in measurement of the individual grain size $\pm 10\%$ of the radius. Average values are reported.

The average velocities for each individual time period and for the linear regression are shown in Figure 18 where the time listed is the time of the initial frame. The average velocities of each interframe period were done to ensure that there was no time dependence of velocity which would indicate either an explosive growth mechanism if there was an acceleration in growth

rate or potentially a phase separation if there was a deceleration. The only instance of there being a significant time dependence of the velocity measurements occurs in the 195°C measurements where the velocity decreases by 23% from the velocity calculated between 25 minutes and 30 minutes and the velocity calculated between 35 minutes and 40 minutes. This is likely not a real time-dependence of the velocity and is more likely that it is due to the limited quality of the images taken during that run as the velocity between 25 minutes and 30 minutes has an exceptionally large standard deviation. At higher temperatures, the grains grew so quickly that it was hard to obtain three frames where the grains were both distinct enough from the background and yet not impinging on other grains. For this reason, the initial frame used often did not have well defined growth boundaries between the amorphous and crystalline phases, so there is likely high uncertainty in the initial grain size measured with several grains likely having a larger initial grain size than measured. This is backed up by Figure 17 where many grains appear to have a consistent slope from the first measurement to the second, but several of the smaller grains size at 25 minutes that seemingly have a large increase to the measurement taken at 30 minutes. Another possible explanation for this jump is that grains have impinged with others causing an apparent increase in the growth of a single grain, but that the separate grains are not visible once impingement occurs.

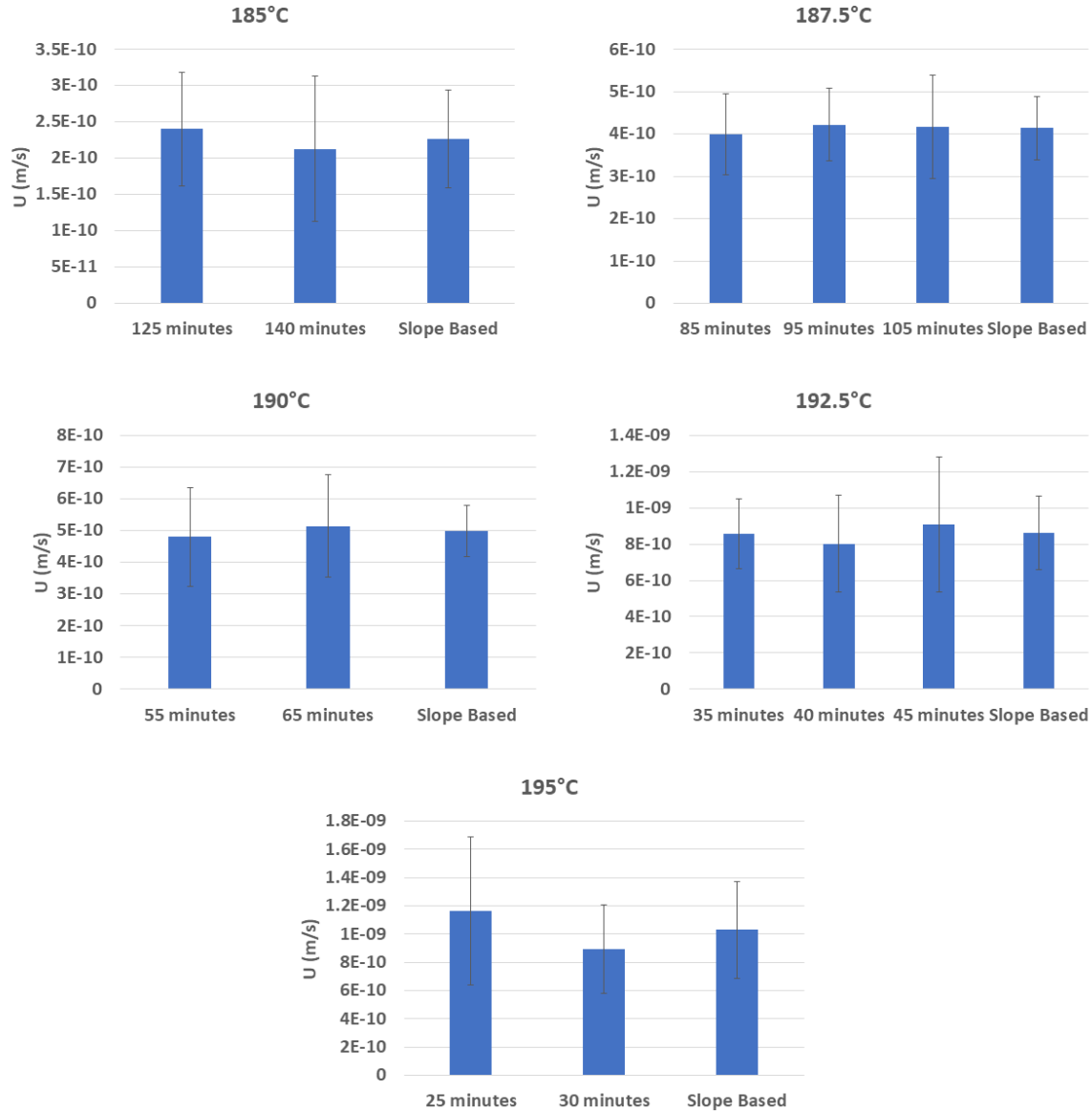


Figure 18: Time based velocities for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ grains. All temperatures appear to have time-independent velocity measurements. Error bars are plus or minus one standard deviation.

Figure 19 shows the slope-based velocities plotted as a function of temperature. Figure 19 b) shows the $\ln(U)$ plotted against $1/k_B T$ and the data is fit with a linear regression. The R^2 value is 0.96 which indicates that the regression is a good fit for the data. The slope is the negative of E_g and calculated for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ is 2.78 eV. The intercept is the $\ln(U_0)$ which when calculated for $\text{Ge}_1\text{Sb}_6\text{Te}_1$, U_0 is 9.72×10^{20} m/s.

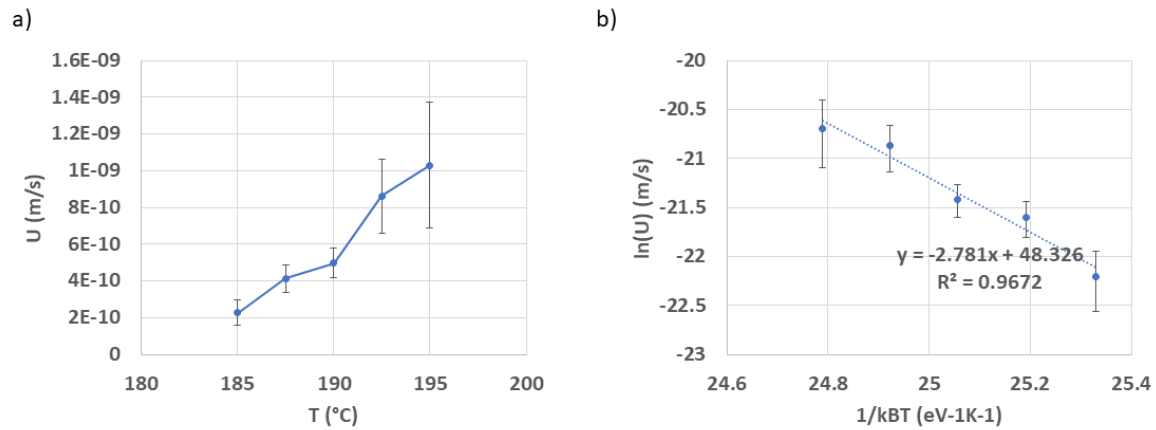


Figure 19: a) Velocity vs temperature for $\text{Ge}_1\text{Sb}_6\text{Te}_1$. b) Arrhenius plot of U vs T . The slope of the plot is the activation energy of crystal growth, E_g , and the intercept is the natural log of the pre-exponential constant U_0 .

4.1.3. JMAK analysis

JMAK analysis was done because despite these materials being growth-dominated the effect of nucleation on overall crystallization rate should not be neglected. In addition, it makes it easier to compare the effectiveness of these growth-dominated materials to nucleation-dominated materials.

Figure 20 shows the thresholded and noise corrected images used to perform the JMAK analysis for the 190°C run and represents a typical image set used.

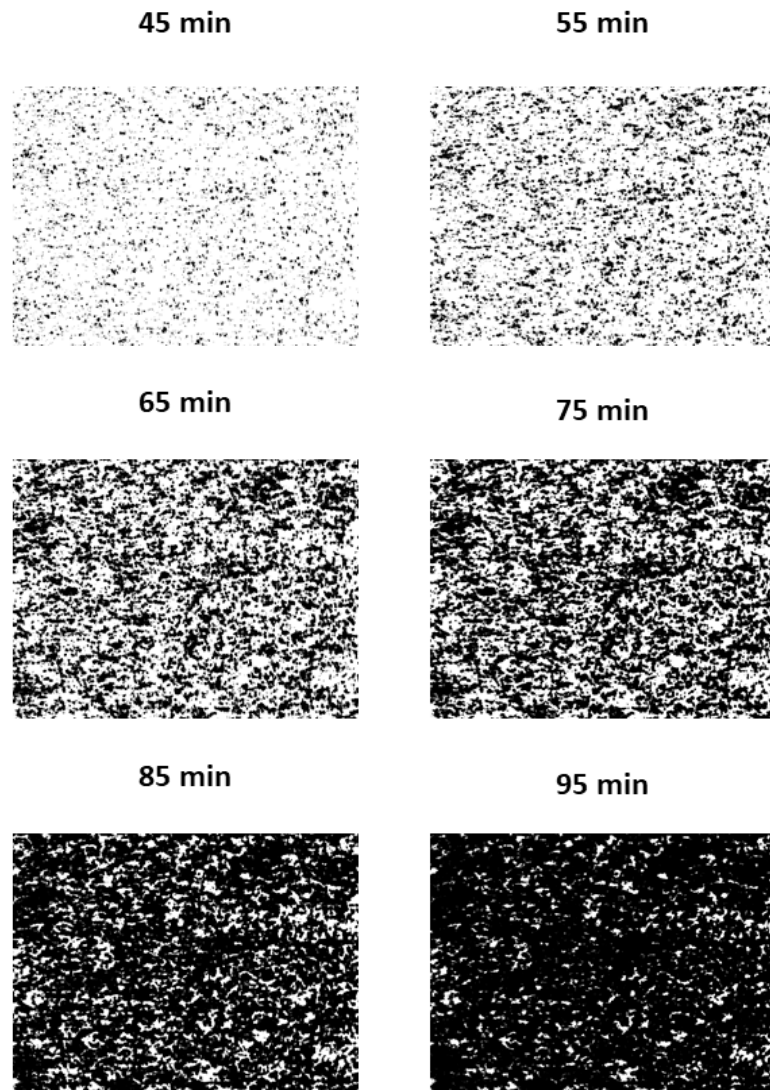


Figure 20: Thresholded noise-corrected images for the 190C $\text{Ge}_1\text{Sb}_6\text{Te}_1$ run that were used in JMAK analysis. The field of view is 275 μm across.

Figure 21 shows the values calculated for t_{inc} by using the average initial grain size and average velocity. The incubation time calculated for either 185°C or 187.5°C doesn't appear to be accurate as incubation time should consistently decrease with increasing temperature due to increased kinetics. This inconsistency should not have a large effect on the final parameters calculated except for n .

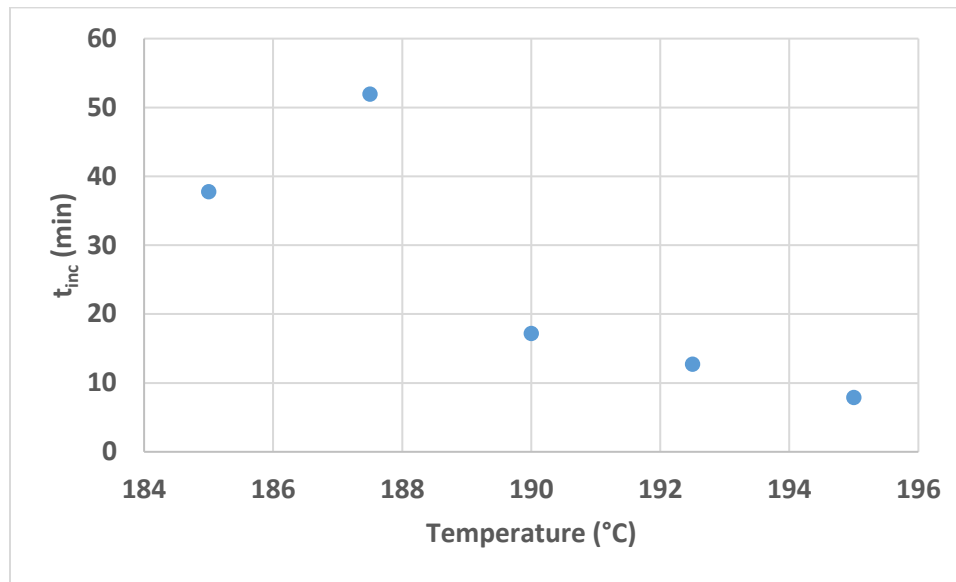


Figure 21: Incubation time as a function of temperature.

The thresholded images are measured to determine percent of area crystallized (χ) and which is plotted as the $\ln(-\ln(1-\chi))$ versus the $\ln(t-t_{inc})$ in Figure 22. A linear regression was applied to the plot and the slope of this regression is the Avrami parameter, n , and the intercept is $n \cdot \ln(k)$. All of the regressions have an R^2 of greater than 0.96 which indicates all of the regressions describe the data well.

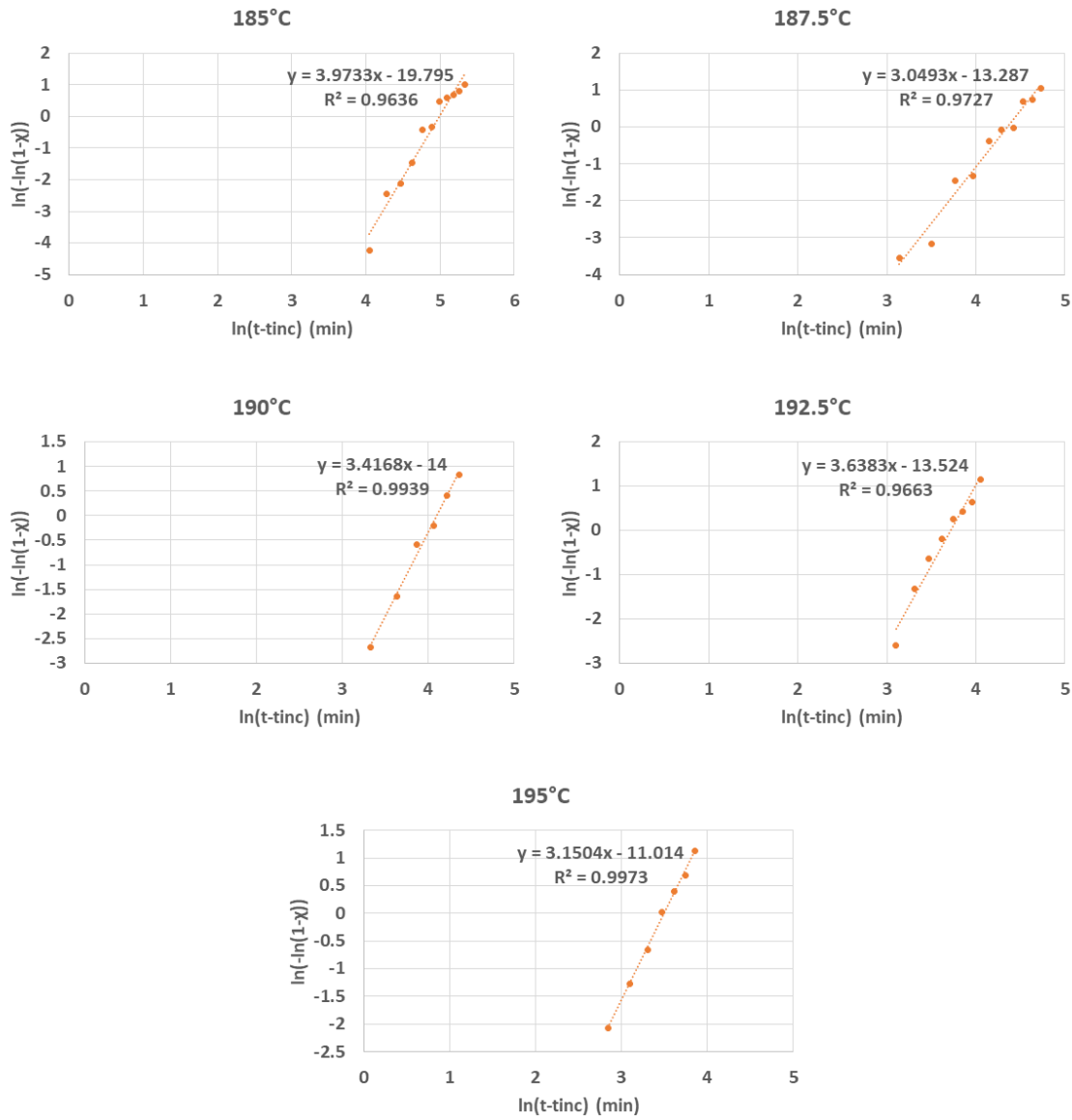


Figure 22: JMAK plots for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ for temperatures from 185C to 195C.

Figure 23 shows the dependence of the Avrami parameter on temperature. If these values aren't mostly independent of temperature then the JMAK data can't be used to get a good E_{comb} as it would indicate a change in mechanism of growth as a function of temperature. Here the values are similar except for 185°C. This may be explained by an inaccurate calculation of t_{inc} at this temperature as a larger incubation time would cause the value of the Avrami parameter to

be lower. All the values are between 3 and 4 which would most likely indicate a growth mechanism of 2-dimensional interface controlled growth.

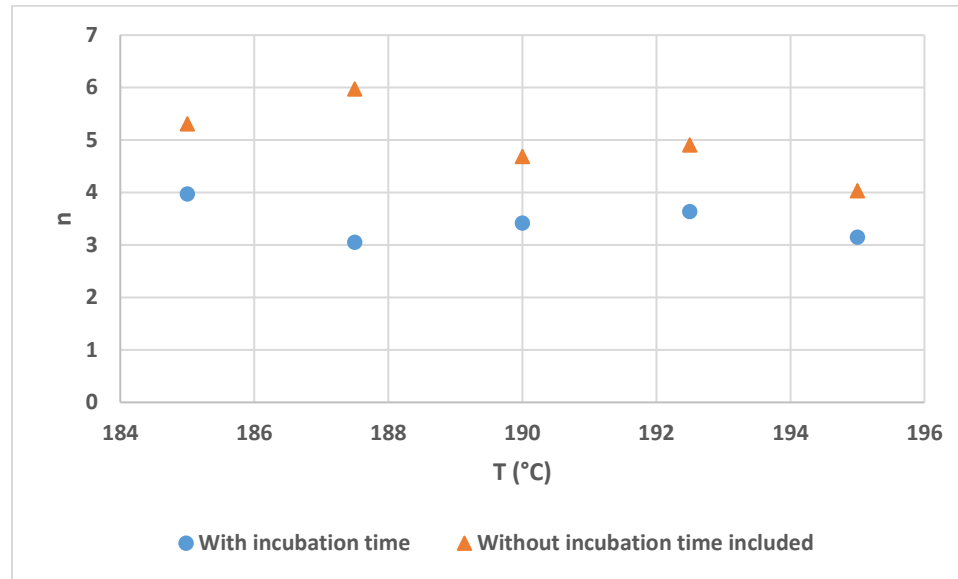


Figure 23: Avrami parameter vs temperature for $\text{Ge}_1\text{Sb}_6\text{Te}_1$. There is not a large variation in value for temperature indicating a constant growth mechanism of mixed 2 and 3 dimensional interfacial growth. The difference between the Avrami parameter calculated with and without an incubation time included is entirely due to the time dependence of nucleation during the transient nucleation period.

The pre-exponential constant, k , is then plotted against temperature as shown in Figure 24.

Figure 24 b) show $\ln(k)$ plotted vs. $1/k_B T$ with a linear regression fit and the negative of the slope is E_{comb} and for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ is 2.67 eV. The intercept is $\ln(k_0)$ and for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ k_0 is $1.98 \cdot 10^{27} \text{ min}^{-1}$.

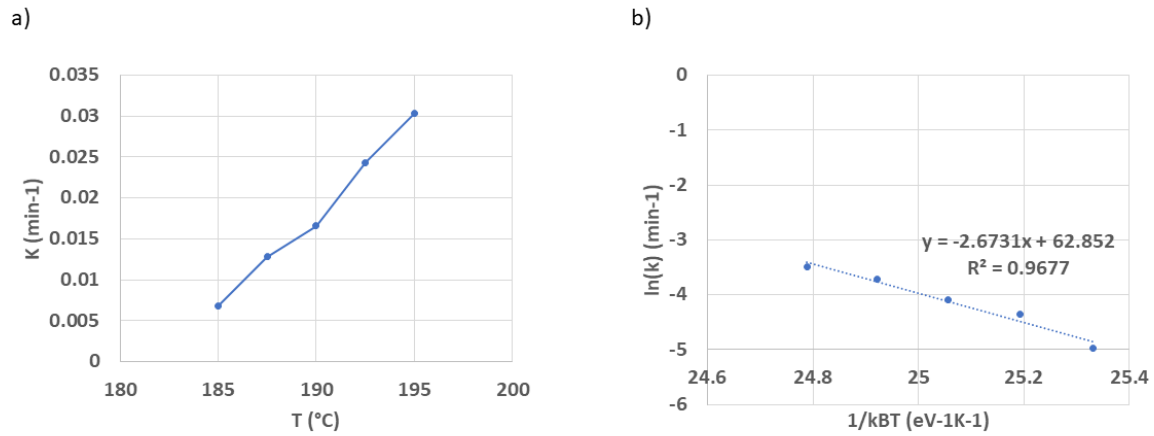


Figure 24: a) Kinetic parameter, k , vs temperature for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ b) Arrhenius plot of k . The slope of this plot is the combine activation energy of crystallization, E_{comb} , and the intercept is k_0 .

4.1.4. The Effect of Illumination on $\text{Ge}_1\text{Sb}_6\text{Te}_1$ Crystallization Kinetics

Experiments were performed with the microscope's illumination source turned off between image capture times because initial tests revealed an increase in crystallinity in a circular area radiating out from the area of observation (Figure 25). Comparisons of growth rate and crystallization rate were made between two runs done at 195°C, one where the light source was left on for the duration of the run and the run previously already shown in this study.

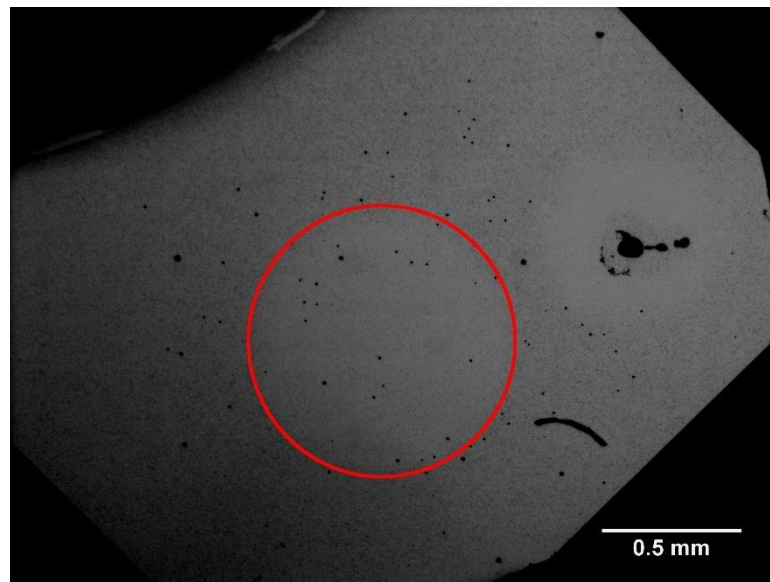


Figure 25: Area of increased crystallinity highlighted in red due to the microscope being on between measurements. Whiter areas indicate crystalline phase and black areas are surface damage.

The crystallization occurred so quickly if the light source was on continuously that there were only two frames that had crystal grains that had not impinged. This made it impossible to calculate a linear regression based velocity. Figure 26 a) and b) allow comparison of grain radius size measurements for the light-aided experiment and the experiment that had minimal exposure to light. Interestingly, at 25 minutes there is not a very large difference between the grain sizes measured with the light exposed compared to those measured with minimal light exposure. There is a much steeper slope for the grain size as a function of time for the light exposed material. Figure 27 shows the velocity of the light exposed material compared to the slope based velocity measured previously. As can be seen the velocity of the growth with the light source on is 85% faster than that measured from the material that had minimal light exposure.

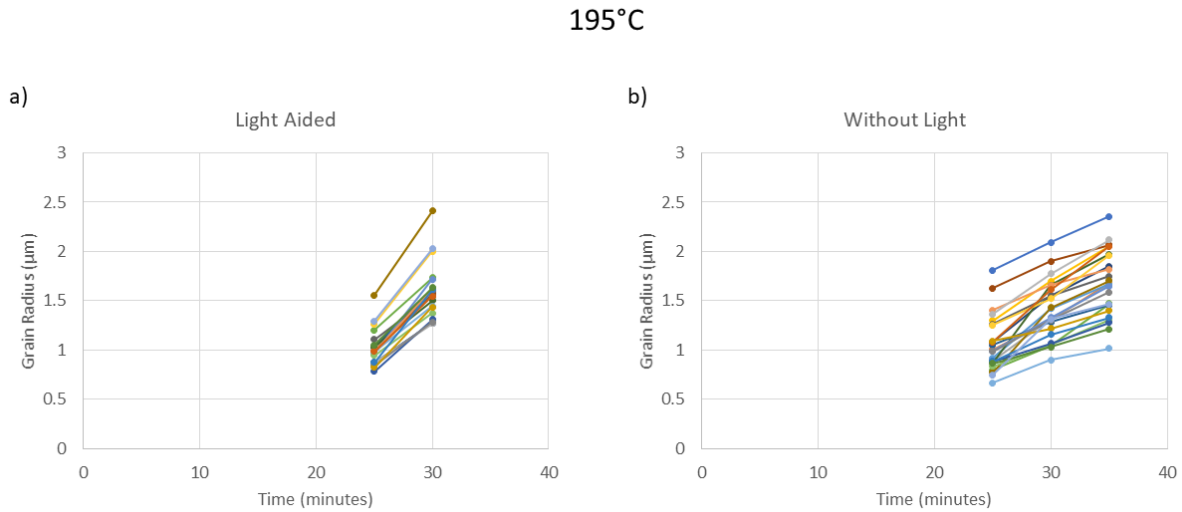


Figure 26: Grain size measurements for $\text{Ge}_1\text{Sb}_6\text{Te}_1$ heated at 195°C with a) the microscope on and b) with the microscope off between images. The grain sizes at 25 minutes are comparable between the two runs but the slope of the grain size is much steeper for a).

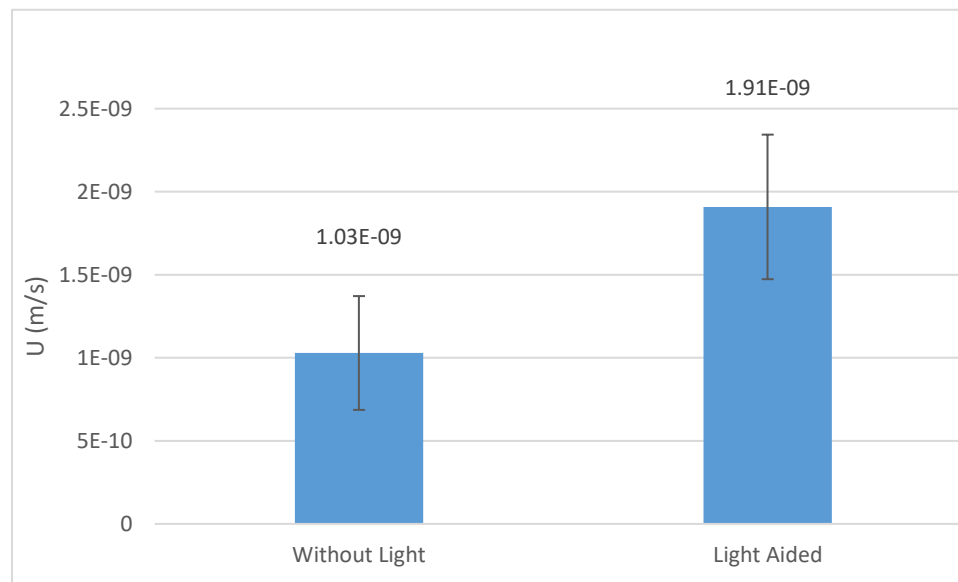


Figure 27: Comparison of the velocities of runs performed at 195°C with and without the light source on. The addition of the light source causes an 85% increase in growth velocity

Incubation time was again calculated extrapolating the time at which average grain size was zero from the initial grain size as described previously. The incubation time increased from 7.9

minutes for the run where the light source was turned off to 16.1 minutes for when the light is turned on. This does not seem like a realistic increase as when performing JMAK analysis the incubation time appears to be nearly identical for both runs because crystallization appears at nearly the same time (Figure 28). This is likely a flaw in the estimation method that is exaggerated by the shorter incubation time in these runs. A major trend to note in Figure 28 is that both runs appear to show crystallization, but the light-aided sample has a much sharper jump in crystallization and completely crystallizes at an earlier time.

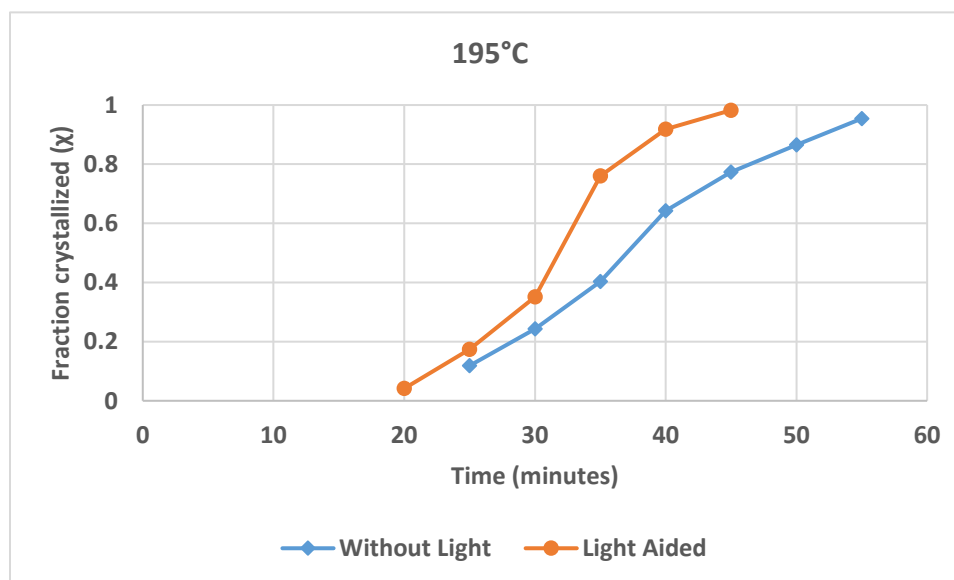


Figure 28: Fraction of area crystallized for runs with and without light. Both runs initiate crystallization around the same time but the sample with the light on crystallized much more rapidly.

Figure 29 shows the JMAK analysis performed for both runs. From this the values in Table VII are calculated. The Avrami parameter is much lower for the light-aided run. This would imply either a change in growth mechanism, growth dimensionality, or both, though it is more likely due to an error in estimation of incubation time. It is unlikely that there is a change in growth mechanism from interfacial controlled to diffusional growth would mean likely mean phase separation and there is no evidence for such a change. Likewise a change in dimensionality would be apparent in a difference in the shape of the grain and again there is no evidence of such a change. The kinetic parameter, k , is 96% higher for the light-aided specimen which is consistent with the growth measurements.

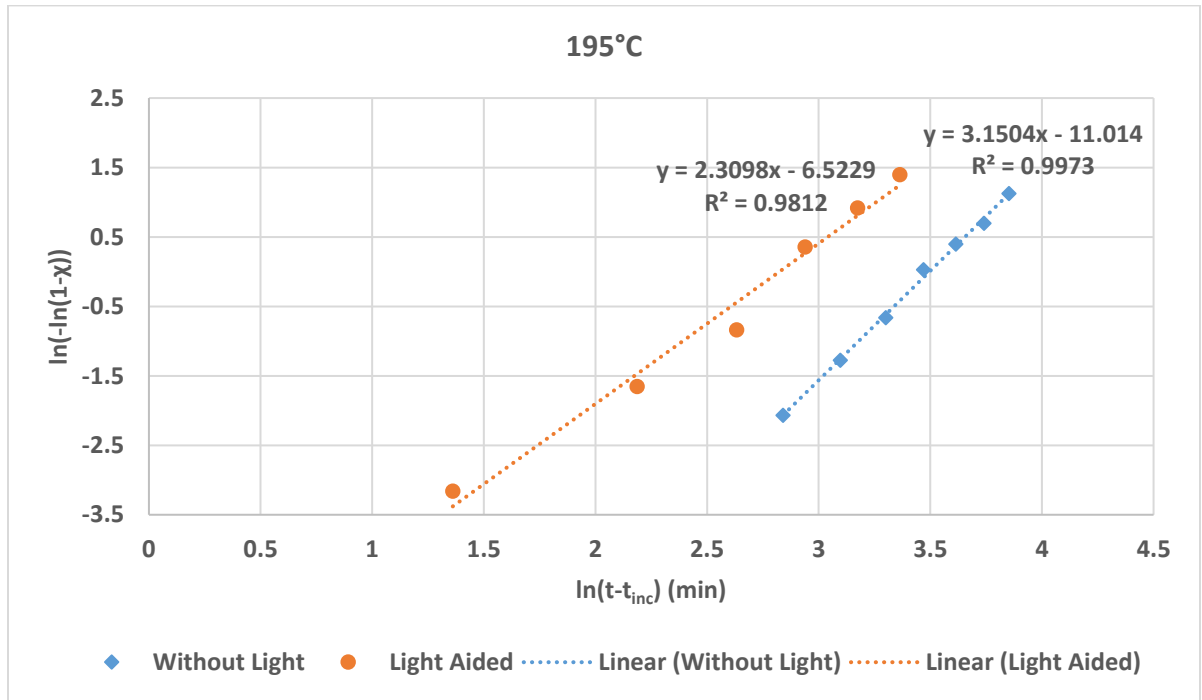


Figure 29: JMAK plot for 195°C runs of $\text{Ge}_1\text{Sb}_6\text{Te}_1$ with and without the light source on. The Avrami parameter for the light-aided growth is far lower and the kinetic parameter, k , is higher than those for the run completed with minimal use of the light source.

Table VII: Calculated parameters for 195°C $\text{Ge}_1\text{Sb}_6\text{Te}_1$ for runs with and without the light source on between frames

	Light-aided	Without Light
U (m/s)	$1.91 \cdot 10^{-9}$	$1.03 \cdot 10^{-9}$
n	2.31	3.15
k (min^{-1})	0.0594	0.0303

4.2. $\text{Ga}_{15}\text{Sb}_{85}$

4.2.1. Image Collection

Images were taken at 50x magnification and at regular time intervals with frame times and temperatures listed in the methods section. Figure 30 shows raw images taken during the run performed at 177.5°C and is representative of a typical set of raw images captured. From these images, it is evident that nucleation and growth start quickly and continue throughout the length of the run, indicating negligible incubation times. This trend is consistently seen throughout all $\text{Ga}_{15}\text{Sb}_{85}$ runs.

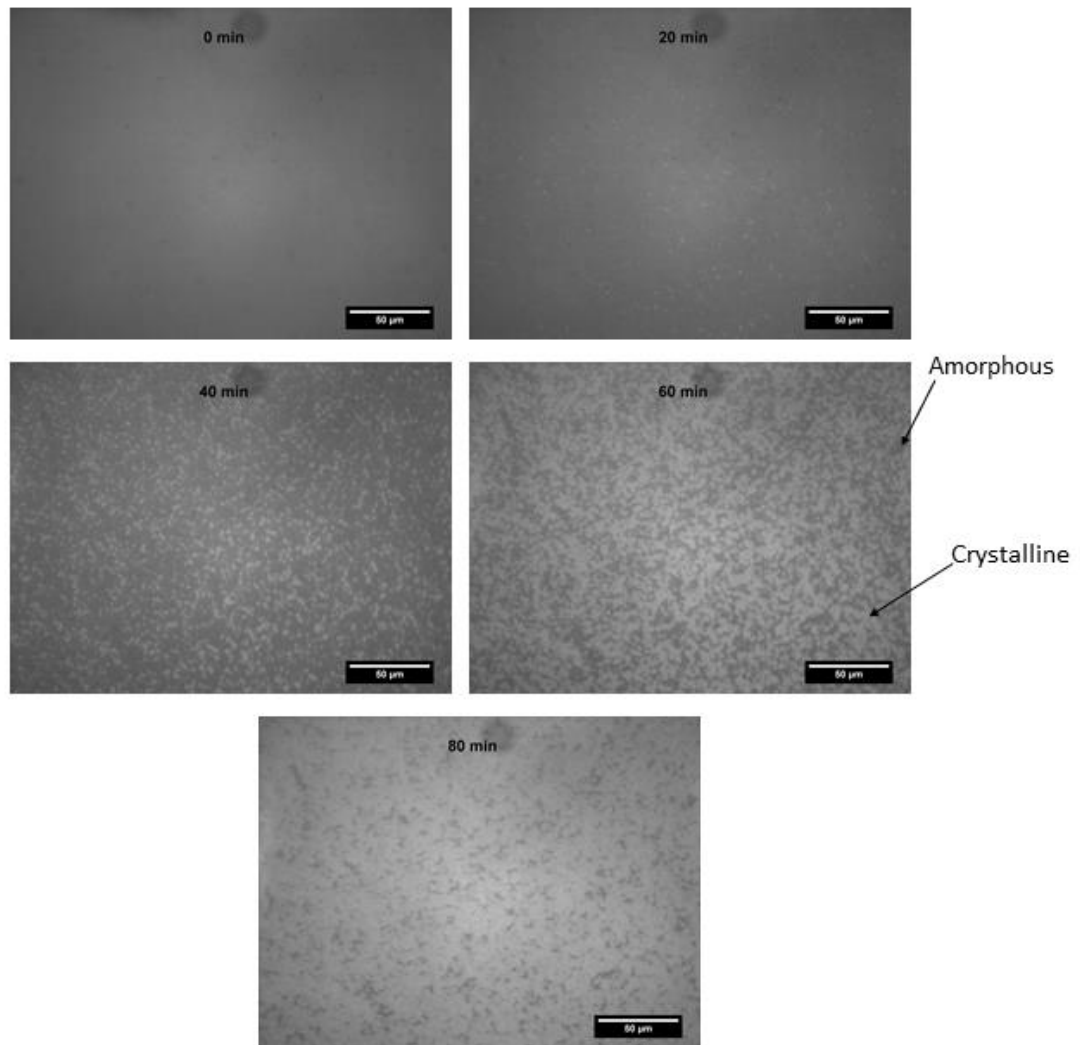


Figure 30: Raw images captured for the 177.5°C $Ga_{15}Sb_{85}$ run. The nucleation of $Ga_{15}Sb_{85}$ appeared at a more constant rate than that of $Ge_1Sb_6Te_1$

4.2.2. Growth Analysis

Growth measurements were done on background subtracted, 16-bit black and white images on grains that had distinct form and had yet to impinge on other grains. Figure 31 shows the set of images used for grain size analysis for the 177.5°C sample and is represents a typical set of images used.

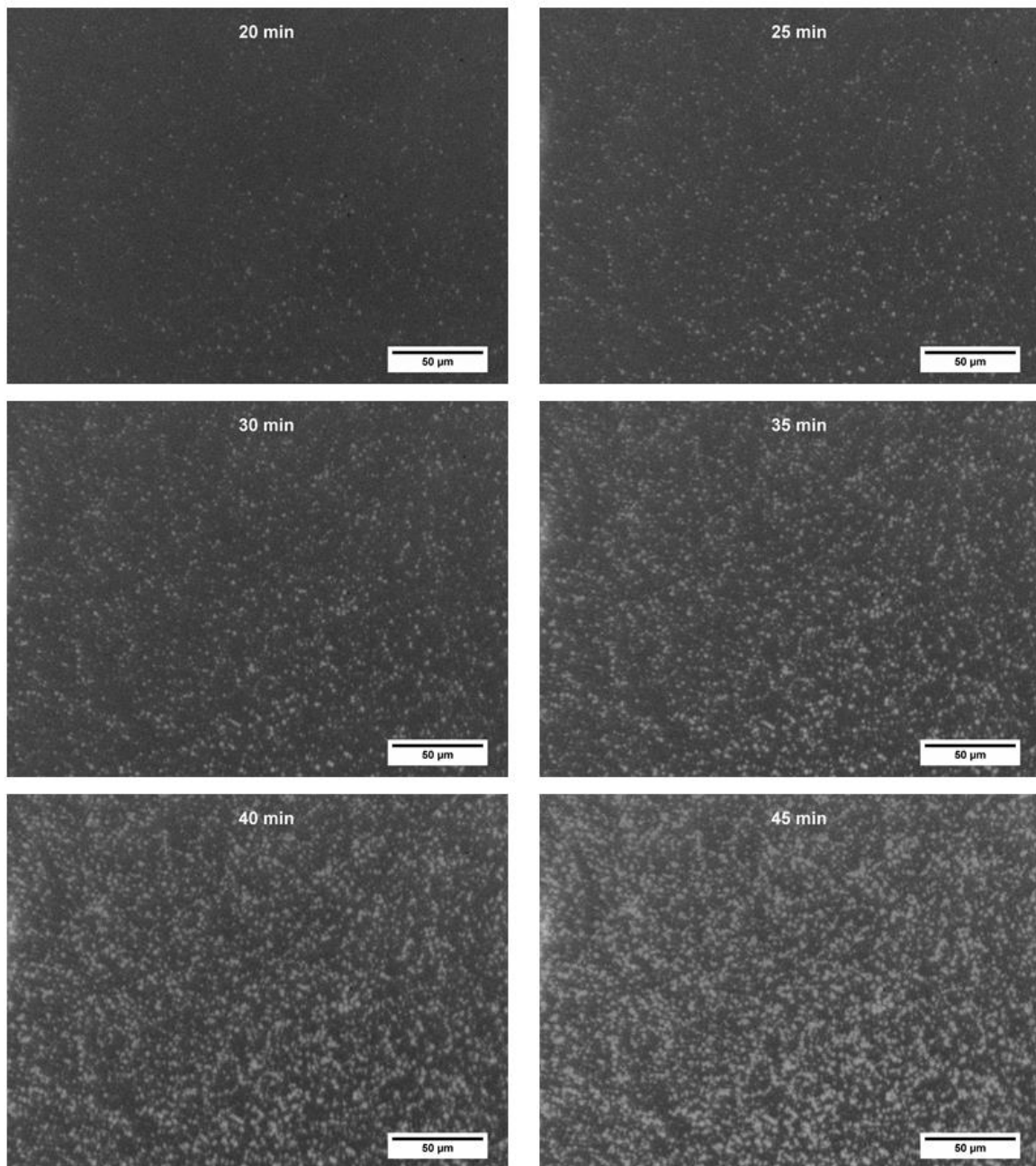


Figure 31: Background subtracted images of the 177.5°C $Ga_{15}Sb_{85}$ run used to measure grain size. This set of pictures represents a typical set of images used.

Figure 32 shows the radius measurements for each grain as a function of time. As was seen with the $Ge_1Sb_6Te_1$ each individual grain may not have had a consistent slope, but when taken

together a slope does appear that is constant with time. The slope does appear less consistent with $\text{Ga}_{15}\text{Sb}_{85}$ than with $\text{Ge}_1\text{Sb}_6\text{Te}_1$. This is likely due to their being less contrast between the crystalline and amorphous forms.

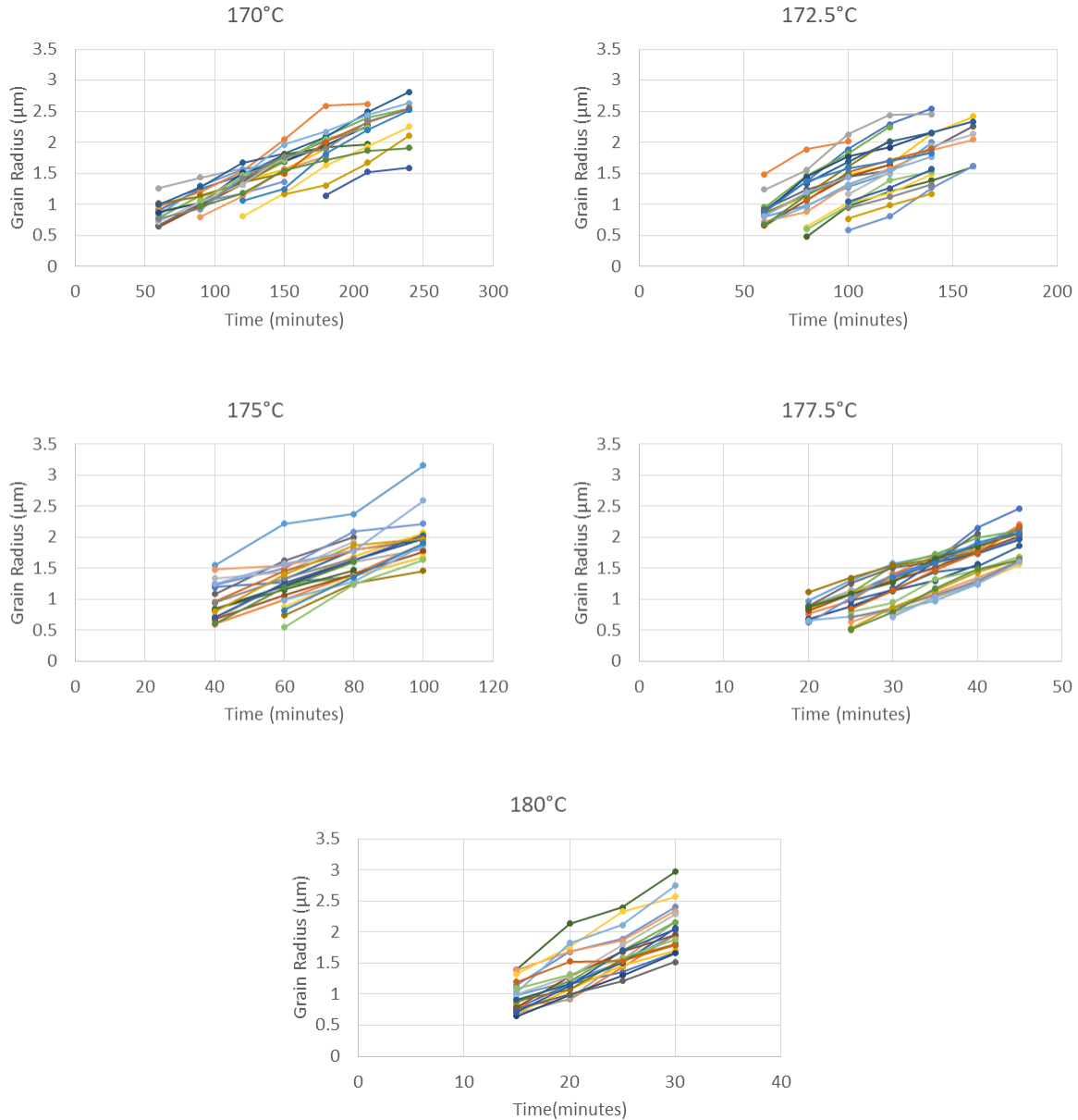


Figure 32: Measured grain sizes for $\text{Ga}_{15}\text{Sb}_{85}$ runs. The frame to frame slope for each grain is not always constant but when taken together a consistent slope appears. The estimated error on the measurements is $\pm 10\%$ the grain radius.

Figure 33 shows the average velocity calculated at each time and by linear regression. This was done to determine if there was a time dependence of velocity on velocity. There is far more variance between times than there was in the $\text{Ge}_1\text{Sb}_6\text{Te}_1$. This is again due to the lower contrast between amorphous and crystalline material in $\text{Ga}_{15}\text{Sb}_{85}$. Interestingly, the two temperatures that have a large variation in velocities, 170°C and 172.5°C , have almost opposite trends. The 170°C specimen had low velocities near grain formation and near grain impingement, whereas the 172.5°C specimen had higher growth velocities near nucleation and impingement. Due to these different trends and the large error bars associated with the measurement, the likely cause of the time dependence trends is more likely due to the difficulty in measuring that occurred at times close to nucleation and to impingement. There is a noticeable increase in velocity with increase in temperature with the 180°C specimen experience nearly an order of magnitude greater crystal growth velocity than the 170°C specimen.

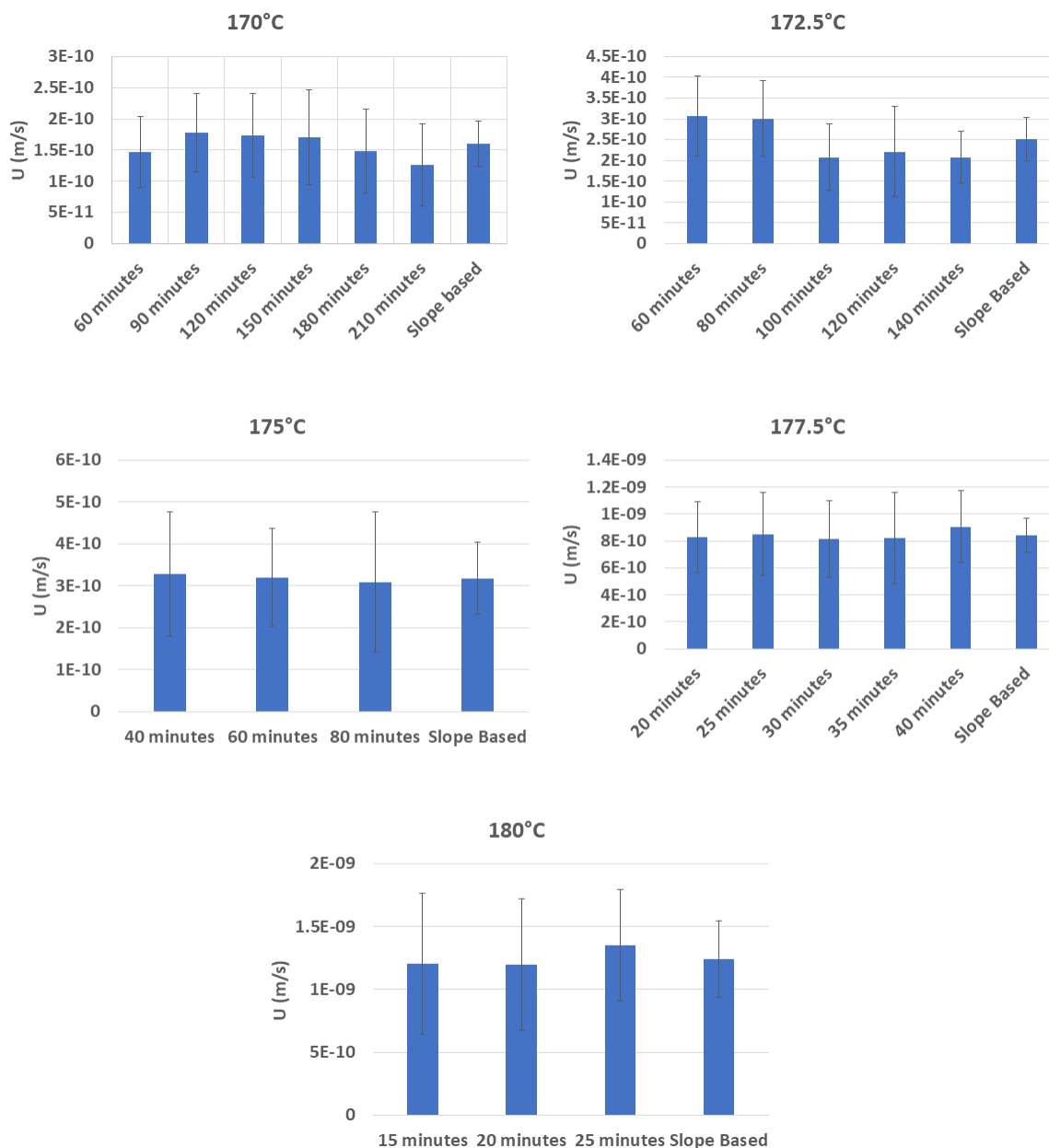


Figure 33: Velocities measured between each time frame. 170C and 172.5C are the only temperatures that don't have a constant velocity as a function of time. The error bars are plus or minus one standard deviation.

Figure 34 shows the slope-based velocities plotted as a function of temperature. Figure 34 b) shows $\ln(U)$ plotted against $1/k_B T$ with a linear regression fit. The R^2 of the linear regression is

0.959 indicating a good fit. From this plot E_g is calculated to be 3.67 eV and U_0 is calculated to be $8.10 \cdot 10^{31}$ m/s.

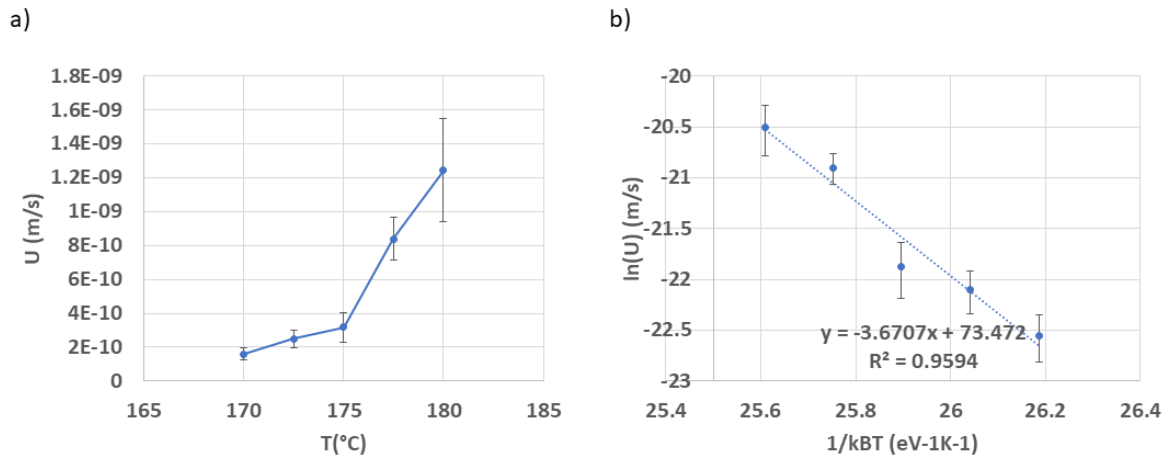


Figure 34: a) Velocity vs temperature for $Ga_{15}Sb_{85}$. b) Arrhenius plot of U vs T . The slope of the plot is the activation energy of crystal growth, E_g , and the intercept is the natural log of the pre-exponential constant U_0 .

4.2.3. JMAK analysis

A JMAK analysis was performed at each temperature. Figure 35 shows an abbreviated version of the thresholded and noise corrected images used in the JMAK analysis performed on the 177.5°C sample. There is a portion on the left of the images that appears to be a long strip of crystallization but is an artifact caused by a window positioned just out of frame causing glare. Any image that had such artefacts was cropped so that the artefacts would not be reflected in the data.

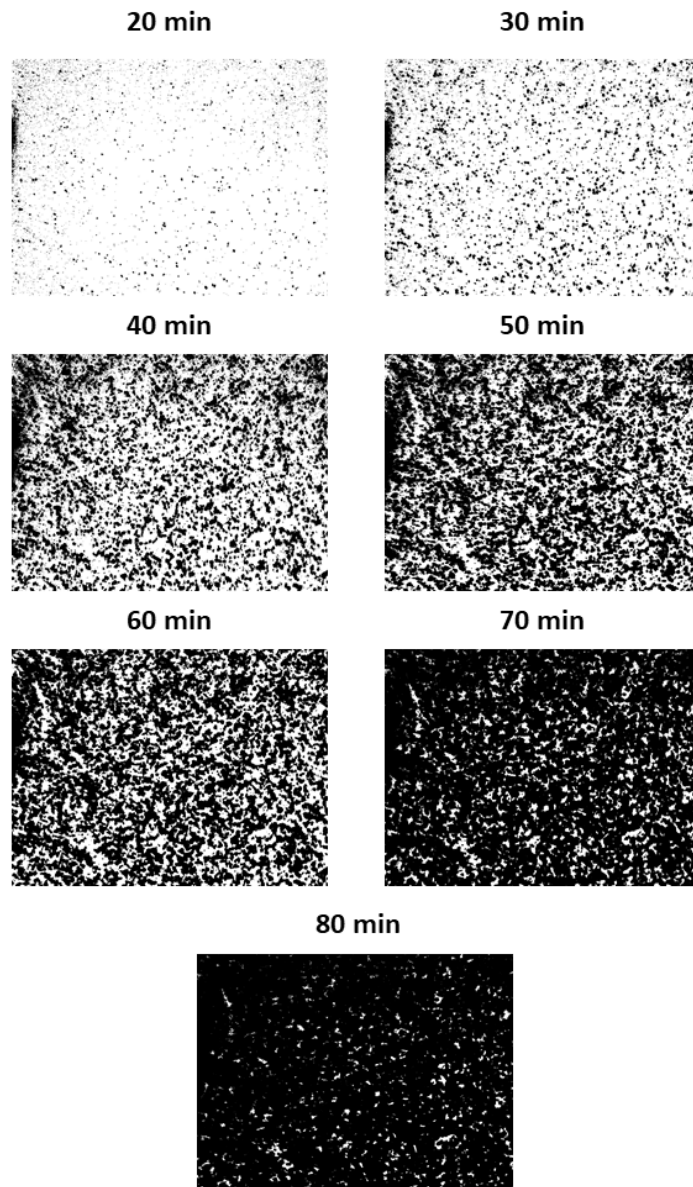


Figure 35: Thresholded and noise-corrected images of the 177.5°C Ga₁₅Sb₈₅ run used to perform JMAK analysis. The field of view is 275 μm across.

The time dependence of the fraction of the area crystallized (χ) is plotted as $\ln(-\ln(1-\chi))$ versus the $\ln(t)$ with a linear regression fit in Figure 36 for all temperatures. R^2 values for all linear fits exceed 0.97 indicating a good correlation to the given equations. Values of k were extracted

from the intercepts of these regressions and plotted as a function of temperature in Figure 37. Figure 37 b) shows the Arrhenius plot of these values with a linear fit. The fit has an R^2 value of 0.98 indicating a good description of the behavior. From this plot k_0 is calculated to be $1.01 \cdot 10^{39} \text{ min}^{-1}$ and E_{comb} is calculated as 3.65 eV.

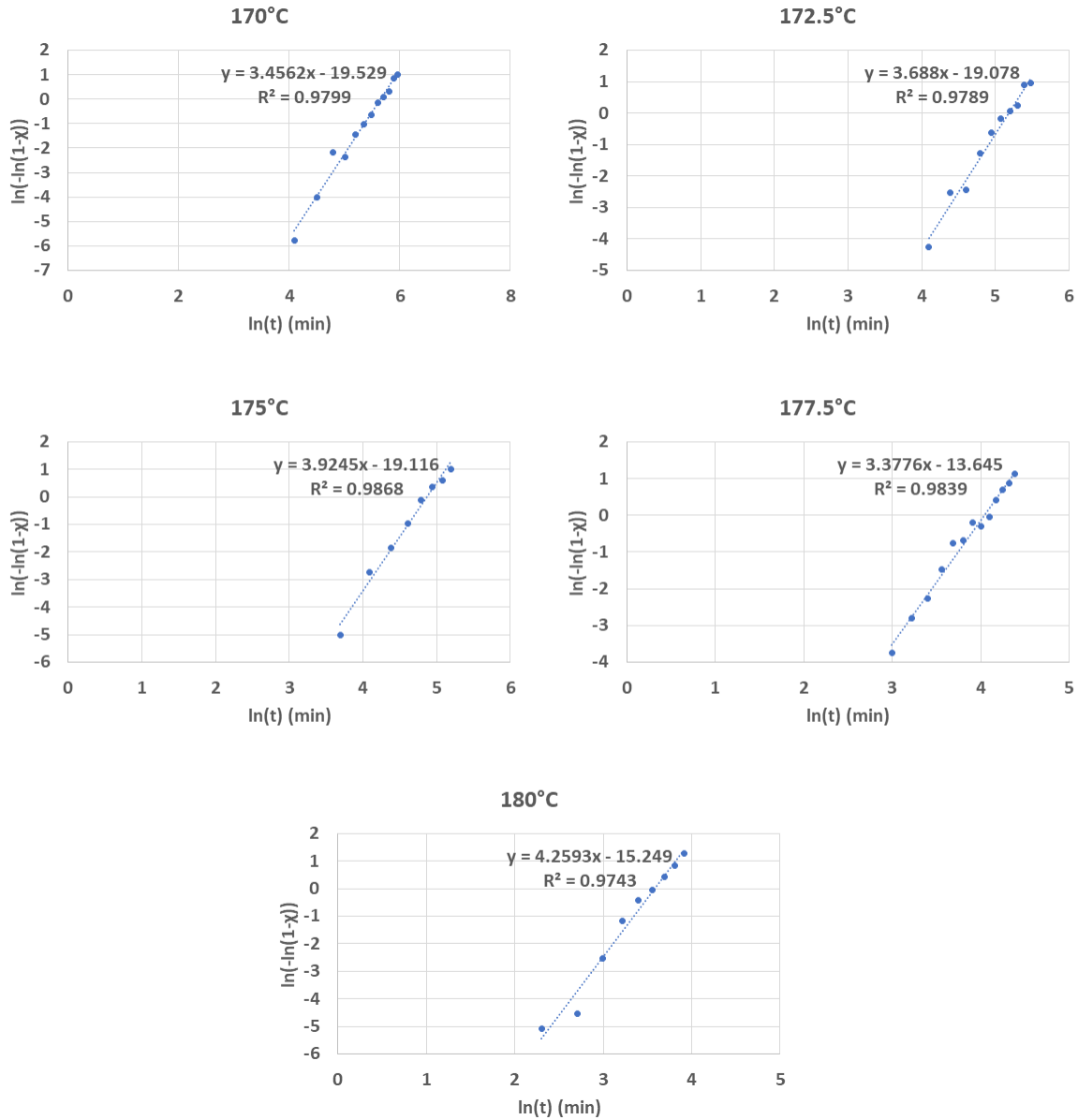


Figure 36: JMAK plots of $\text{Ga}_{15}\text{Sb}_{85}$ for each temperature. The slope of each plot is the Avrami parameter, n , and the intercept is $n \cdot \ln(k)$.

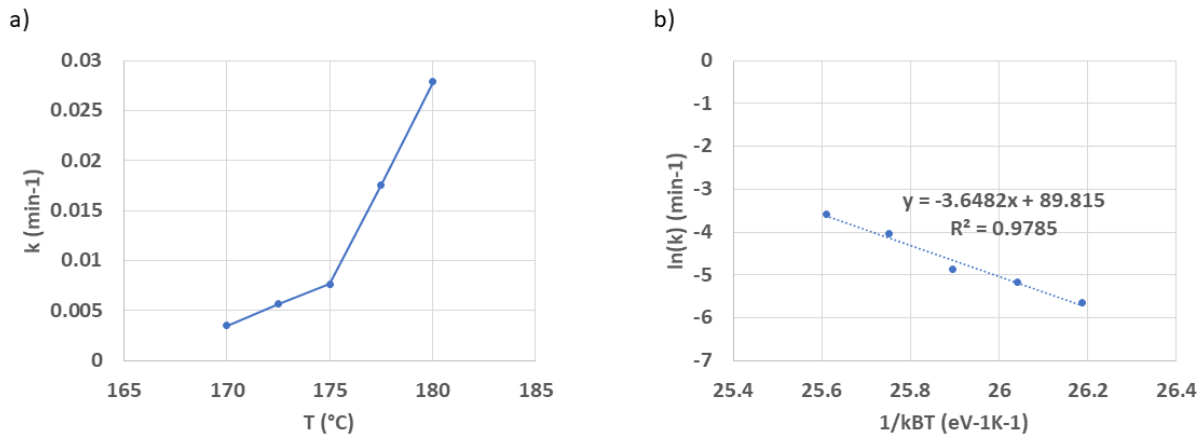


Figure 37: a) Kinetic parameter, k , versus temperature for $Ga_{15}Sb_{85}$. b) Arrhenius plot of kinetic parameter. The slope of this plot is the negative of the combined activation energy of crystallization (E_{comb}) and the intercept is k_0 .

The Avrami parameter, n , is plotted as a function of temperature to determine if there is an apparent change in growth mechanism with temperature (Figure 38). There does appear to be a general increase in the value of n with an increase in temperature culminating in a calculated value of n at 180°C that is physically meaningless as it exceeds the maximum value for ideal crystallization in bulk materials.

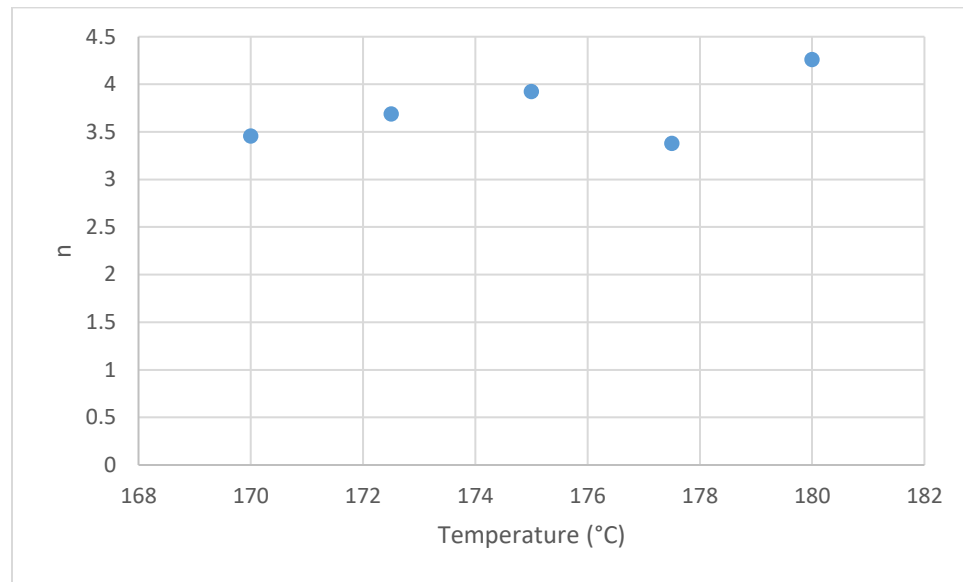


Figure 38: Avrami parameter vs temperature for $Ga_{15}Sb_{85}$. There is a loose trend of increasing Avrami parameter with increasing temperature.

5. Discussion

5.1. Comparison of U(T)

The growth rate for GST161, $Ga_{15}Sb_{85}$, $AlST^{15}$ and $GeTe^{29-30}$ was extrapolated for the temperature range 25°C-200°C (Figure 39). $Ga_{15}Sb_{85}$ has the lowest growth rate at ambient temperature up until around 150°C where it becomes faster than GST161. For the entire temperature range both GST161 and $Ga_{15}Sb_{85}$ have slower growth rates than AIST and GeTe however $Ga_{15}Sb_{85}$ shows a much stronger temperature dependence of growth rate and has a similar growth rate at higher temperature ranges to that of GeTe and AIST.

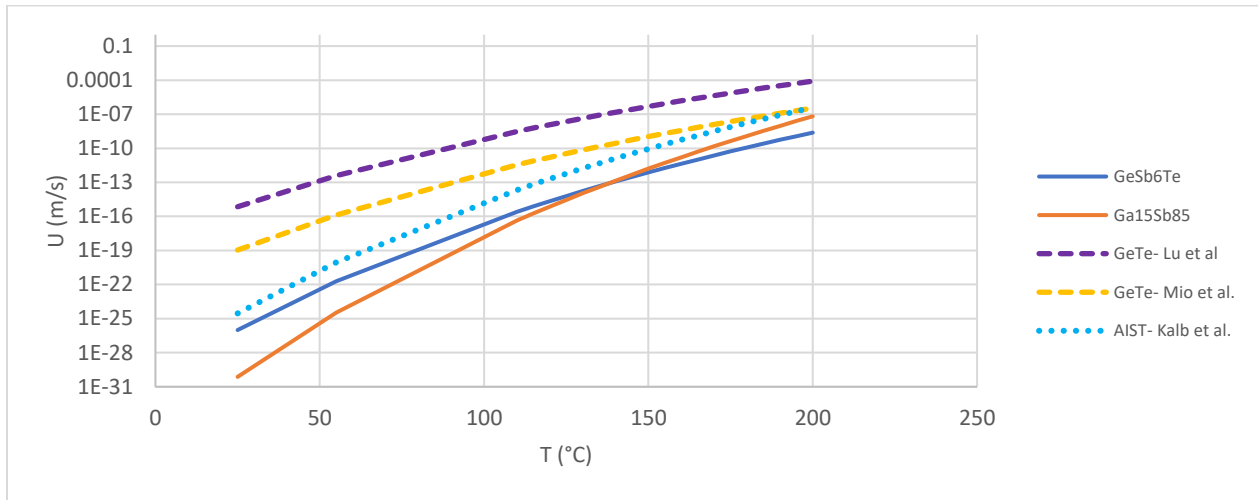


Figure 39: Growth rate of GST161, $Ga_{15}Sb_{85}$, GeTe and AIST extrapolated for the temperature range 25°C to 200°C. Both GST161 and $Ga_{15}Sb_{85}$ have lower growth rates in this range than the prototypical PCMs, however $Ga_{15}Sb_{85}$ exhibits a much faster increase than any of the other materials.

5.2. Comparisons of Kinetic Parameters

Both U_0 and E_g affect the low temperature growth rate of a material in different ways. U_0 is essentially the growth rate at an infinite temperature assuming that there were no thermodynamic barriers or melting to take into consideration. Changing U_0 shifts the growth up or down as a function of temperature but does not change the slope. E_g on the other hand is related to the rate at which the growth rate changes with changing temperature.

5.2.1. $Ge_1Sb_6Te_1$

$Ge_1Sb_6Te_1$ values of U_0 and E_g are typical of growth-dominated PCM materials. Since activation energies are typically very large for these materials, values of U_0 tend to also be equivalently large since crystallization occurs at lower temperatures. Values for the kinetic constants are shown compared to values of the prototypical growth-dominated materials, AIST and GeTe, as well as to high antimony alloys in Table VIII. Both U_0 and E_g are between the values for GeTe and AIST with GeTe having lower values and AIST having higher. E_g is the general barrier to growth and a higher E_g would generally mean slower growth, but a higher U_0 can offset this. Comparing $Ge_1Sb_6Te_1$ to GeTe is a balancing act as E_g for GeTe is lower indicating it has a faster growth rate but GeTe has a generally lower value for U_0 which would slow down the growth rate. The JMAK derived activation energy is in line with other high antimony alloys like AIST and $Ge_{15}Sb_{85}$.

Table VIII: Kinetic parameters values for GST161 and select other growth-dominated PCMs

Material and Source	Ge ₁ Sb ₆ Te ₁	AIST ¹⁴⁻¹⁵	GeTe ²⁷ , 29-31, 33	Ge ₆ Sb ₉₄ ⁵⁰	Ge ₁₀ Sb ₉₀ ⁵⁰	Ge ₁₅ Sb ₈₅ ²⁰	Ge ₂₂ Sb ₇₈ ²⁰
E _g (eV)	2.78	2.90	1.45- 2.27	1.7	5.5	-	-
U ₀ (m/s)	9.72*10 ²⁰	3.025*10 ²⁴	5.9*10 ¹⁴ - 7.0* 10 ¹⁴	-	-	-	-
E _{comb} (eV)	2.67	2.7	1.7	-	-	2.46	3.59
k ₀	1.98*10 ²⁷	-	-	-	-	-	-
n	3.15-3.97	-	4.0-4.5	-	-	-	-

The Avrami parameter indicates growth mechanism. There are multiple different approaches to trying extract information from the Avrami parameter when transient nucleation is involved. For data where nucleation does not appear for a period of time, such as in the GeSb₆Te experiments, an incubation time is often used to correct for the initiation of nucleation. Other studies that have used materials that have shown transient nucleation ignore any transient time and make assumptions about the dimensionality of growth and assume that if the Avrami parameter is higher than expected that it is due entirely to the time dependence of nucleation.²⁹ The results of the current work show that both of these methods have their merits and drawbacks. The incubation time method is useful as it allows for estimation of elements of growth such as dimensionality and if the growth is diffusion controlled or not, but is limited by the fact that it can only really be used if the transient effect is an incubation mechanism as opposed to a ramp-up mechanism and by the fact that estimation of incubation time is unprecise and a small change in estimation can affect the calculated Avrami parameter by a significant amount. The method of assuming dimensionality of growth is useful in determining time dependence of the nucleation rate during the transient time, but is hindered by the fact

that it requires assumptions about growth characteristics and if the measurements extend past the transient time the exponent is not going to be accurate. In the GeSb_6Te experiments the Avrami parameter fluctuates wildly when not calculated with an incubation time with a lowest value of 4.03 at 195°C and a maximum value of 5.97 at 187.5°C. Lu *et al.* also found Avrami exponents greater than 4 when calculating n for GeTe.²⁹

Even though illumination of the GeSb_6Te sample almost doubled both crystal growth rate and crystallization rate, it does not appear this effect was thermally induced. The reasoning behind this statement is two-fold. The illumination source for the microscope is an LED source, a source that generates relatively small amounts of heat, that is located far away from the imaging area which would mean it's unlikely that heat was directly input into the system by the illumination system as that would mean that the entire sample would experience increased crystallization. It is also unlikely that the light induced a thermal excitation in the area that was being focused as the incubation time has a distinct decrease with increasing nucleation time whereas the illumination of the sample actually increased the calculated incubation time. A reduction in incubation time would be expected at the low temperatures of these experiments because increasing temperature will increase the kinetics of the specimen allowing for faster relaxation of the material. This means that it is likely an electronic excitation of the material that increases the crystallization of the material. The electronic excitation of this material would fall within the range of blue to violet light which is entirely reasonable to expect to be emitted from a microscope light source and is near where the wavelength of maximum absorption would be found for other PCMs.⁵ A literature search for this effect in other PCMs yielded no results as all papers found referred only to laser crystallization of PCMs, where significant specimen heating is expected.

5.2.2. $\text{Ga}_{15}\text{Sb}_{85}$

The values of E_g , U_0 , E_{comb} , and k_0 for $\text{Ga}_{15}\text{Sb}_{85}$ calculated in this work are compared to values for similar materials and to values for the prototypical growth-dominated materials AIST and GeTe in Table IX. The values of E_g and U_0 for $\text{Ga}_{15}\text{Sb}_{85}$ are significantly higher than those for both AIST and GeTe. The value calculated for E_{comb} in this work is slightly higher than that previously calculated by Van Pieterse *et al.*²⁰ using reflectivity measurements but certainly within reason considering differences in substrate and capping layer. The values of both E_{comb} and k_0 are very

similar to those measured for $\text{Ga}_{13}\text{Sb}_{87}$ by Chang et al.¹⁸, but are significantly different than those measured for $\text{Ga}_{16}\text{Sb}_{84}$ calculated in the same study. The Avrami parameters calculated by Chang *et al.*¹⁸ for $\text{Ga}_{13}\text{Sb}_{87}$ and $\text{Ga}_{16}\text{Sb}_{84}$ are lower than those calculated in this study (1.91 for $\text{Ga}_{13}\text{Sb}_{87}$ and 1.16 for $\text{Ga}_{16}\text{Sb}_{84}$ compared to 3.38-4.26 calculated for $\text{Ga}_{15}\text{Sb}_{85}$). There could be many reasons for this including: film thickness, unaccounted transient nucleation in $\text{Ga}_{15}\text{Sb}_{85}$, or different methods of measurement (DSC vs optical microscopy)

Table IX: Kinetics Parameters of $\text{Ga}_{15}\text{Sb}_{85}$ and other selected growth-dominated materials

Material and Source	This work	$\text{Ga}_{15}\text{Sb}_{85}$ ²⁰	$\text{Ga}_{13}\text{Sb}_{87}$ ¹⁸	$\text{Ga}_{16}\text{Sb}_{84}$ ¹⁸	AIST ¹⁴⁻¹⁵	GeTe ^{27, 29-31, 33}
E_g (eV)	3.67	-	-	-	2.9	1.45-2.27
U_0 (m/s)	8.10×10^{31}	-	-	-	3.025×10^{24}	5.9×10^{14} - 7.0×10^{14}
E_{comb} (eV)	3.65	3.34	3.3	6.9	2.7	1.7
k_0	1.01×10^{39}	-	3.1×10^{35}	1.6×10^{70}	-	-
n	3.45-4.26	-	1.91	1.16	-	4.0-4.5

6. Conclusions and Future Work

Overall this work has shown that the values of E_g , U_0 , E_{comb} , and k_0 for the phase change memory materials, GeSb_6Te and $\text{Ga}_{15}\text{Sb}_{85}$ are similar to other growth-dominated materials. GeSb_6Te has values of E_g , E_{comb} , and U_0 that fall between those of GeTe and AIST. $\text{Ga}_{15}\text{Sb}_{85}$ has values of E_g , E_{comb} , and U_0 that are above those of GeTe and AIST but fall around those found in other gallium antimonide materials that contain high antimony content. Additionally it was discovered that the illumination of the microscope increased the crystal growth velocity of GeSb_6Te by 85% at 195°C. Perhaps more importantly than comparing these two materials to other PCMs, this work has established the crystallization kinetics parameters of low temperature growth that can now

be paired with studies in the intermediate and high temperature regimes of these materials. Winseck *et al.*³⁸ has already established the high temperature growth rate of GeSb₆Te however there has been no work in the intermediate temperature regime. This can be accomplished by using ultrafast DSC. In addition to needing the intermediate regime measured using ultrafast DSC, Ga₁₅Sb₈₅ also requires the high temperature region probed. This can be done using dynamic transmission electron microscopy. Additionally, if these materials are to ever be used in an actual device more extensive testing needs to be done on the durability of the phase transformation by cycling the transition.

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