Crystallization in Sugar Glass using Home-Built Laboratory Equipment

Sarah Horst, Department of Materials Science and Engineering, Lehigh University
Advised by Dr. William Heffner, IMI-NFG, Lehigh University

July 31, 2009

Abstract:

Experiments were designed so that any person with a desire to study glass can do so in an easy, affordable manner. These low cost experiments utilize sugar glass, a.k.a. hard candy, as the material system and home-built experimental apparatus constructed from household items. By utilizing both accessible and affordable materials, a wide range of students may experience a hands-on introduction to some of the exciting aspects of glass science. The specific topic of crystallization was chosen because of its importance in glass and material science, as well as its relevance to applications in both glass and glass-ceramics. The primary objective of our crystallization study was to measure the temperature dependence of crystallization, both nucleation and growth, in the sucrose-water-corn syrup system. Some of the procedures developed include the methods for: making sugar glass, developing appropriate sample methodology, measuring the crystal fraction and determining the peak growth temperature. Equipment developed for the studies include: a low cost sample heater made from cans and a light bulb heat source, a dimmer switch temperature control, cookie jar desiccators, and even a microscope hot stages for watching crystals grow and observing crystallization dynamics. The research showed that crystal growth in this sugar glass system has a maximum at 120°C, and the crystal growth occurs throughout the bulk of the samples, and not primarily at the substrate surface. However, intentionally scratched glass substrates result in a dominance of surface crystallization. Multiple crystal morphologies were observed, and the temperature dependence of their formation is an open question for future low-cost experiments with this system. These experiments and results will be posted on the website of the International Materials Institute for Glass for access by individual or classroom use.

Support provided by the International Materials Institute for New Functionality in Glass (NSF–IMI, DMR-0409588) and the National Science Foundation

1. Introduction

Glass can be difficult to study in a high school or home laboratory as much of it requires the use of high temperature furnaces and other special laboratory equipment due to high melting and transition temperatures. In order to overcome this setback the low temperature glass made from heating a water, sugar, corn syrup mixture to approximately 150°C was used for experimentation. The sugar glass used was approximately 2/3 sugar and 1/3 corn syrup by weight.

Glass crystallization is an important area of study because many glass applications require the complete inhibition of crystallization, while others use carefully controlled crystallization to improve properties. Crystallization in the sugar glass matrix is effected by many elements including water content, amount of corn syrup, humidity, and temperature. Understanding how to inhibit or control crystallization in sugar glass is important for confectioners and very analogous to other glasses.

Crystallization occurs in two steps: nucleation, the appearance of new particles in the matrix, and growth, the process by which these particles increase in size. In order for homogeneous nucleation (or nucleation throughout the bulk of the material) to occur, an activation free energy, $\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_E - T)^2}$ must be overcome. This activation free energy decreases as temperature decreases, meaning a temperature below the melting temperature will allow nucleation to occur more readily. Furthermore, the nucleation rate, in nuclei per unit volume per second, $\dot{N} = K_1 K_2 K_3 [\exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{G_d}{kT}\right)]$, where K_1, K_2, and K_3 are constants that depend on the system. Figure 1 is a schematic plot of the nucleation rate versus temperature that includes curves for each exponential in the equation. Note that the nucleation rate peaks at some temperature below T_m. (Callister, 2008)

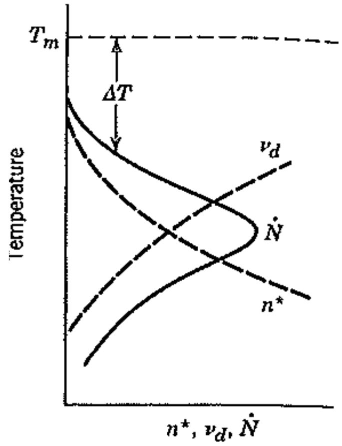


Figure 1. Schematic plot of temperature, includes curves for number of stable nuclei, n*, and frequency of atomic attachment versus temperature. (Callister, 2008)

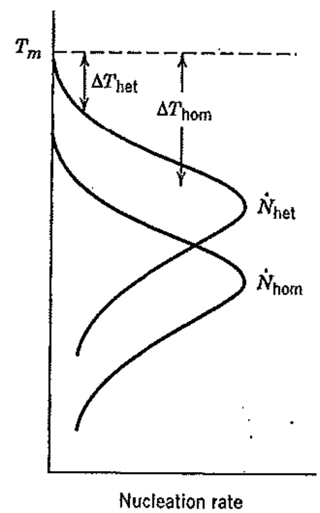
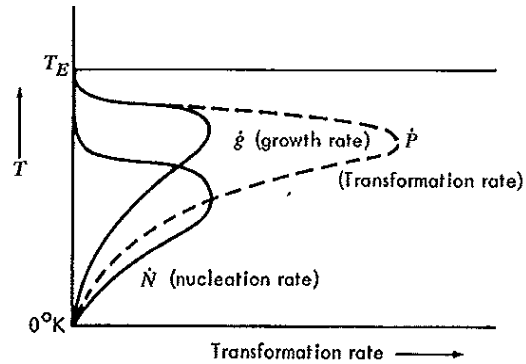


Figure 2. Schematic for nucleation rate versus temperature for both homogeneous and heterogeneous nucleation. (Callister, 2008)

Most nucleation, however, will occur heterogeneously (nuclei form on preexisting surfaces or interfaces) because the activation free energy is lowered due to a reduction in the surface free energy, γ. The lowering of required free energy results in a shift of the nucleation rate curve upward in temperature, meaning that heterogeneous nucleation can occur at higher temperatures as shown in Figure 2. (Callister, 2008)

Once a nuclei becomes stable it will begin the growth portion of crystallization. Growth occurs by atomic diffusion and the growth rate is $\dot{G} = Cexp(-\frac{Q}{kT})$. (Callister, 2008) A schematic plot shown in Figure 3 includes the growth and nucleation rate curves, as well as a curve showing the overall transformation rate with temperature. Note again that there is a maximum for the growth rate at some temperature below T_E. Usually the maximum temperature for the growth rate is higher than the maximum temperature for the nucleation rate because the diffusion rate is more temperature sensitive. (Barrett, Nix, Tetelman, 1973)

Figure 3. Schematic of nucleation rate, growth rate, and transformation rate versus temperature. (Barrett, Nix, Tetelman, 1973)



The objectives of this research were to determine the temperature at which crystallization occurs most readily, to understand the process by which the crystals are forming, and to do using easy and reproducible experiments.

2. Methods and materials

Sugar glass was made with a mixture of sugar and corn syrup in dry weigh ratio of 2/1, respectively. The mixture included some water (~1/4 the weight of the corn syrup) to ensure the sugar dissolved. The solution was heated to approximately 150°C until a sufficient amount of water evaporated so that drops of the mixture into cold water made a cracking sound. Samples were initially made by dropping the mixture onto glass microscope slides and using washers as a spacer for the top slide. It was later discovered that if drops were made sufficiently small they did not need a top slide and would act the same when tested. The process was further refined with the introduction of a hollow glass rod which helped to create more uniform drops and thin cover slips to form small flat samples. The samples were stored in jars with a rubber seal that contained Drierite to remove humidity.

To study crystallization rates a heater was designed using basic materials such as a coffee can and light bulb and a dimmer switch for temperature control. For more on the heater see Appendix A. The sugar glass samples were labeled and set on the heater at 80, 90, 100, 110, 120, 130, 140, and 150°C to encourage crystallization. For the first several experiments, 20 minutes at temperature was sufficient time to get a measureable amount of crystallization, but later experiments required 40 minutes or more to grow measureable crystals. This difference is a result of the extreme variation between samples and batches of glass. Six samples were studied at each temperature. After the heat treatment was complete, crossed polarizers were used to examine the crystals. For the first four tests a Digital Blue QX 5 Computer Microscope was used to take pictures of the samples. For the final two tests a Nikon light optical microscope using transmitted light was used in conjunction with a basic digital camera to take pictures. All of the images were analyzed using freeware called ImageJ. For accuracy, the procedure for the measurement was repeated several times for each image. For more on ImageJ and the procedure for analyzing the images see Appendix B. Plots of temperature vs. area fraction of crystals were created to determine at which temperature the crystallization rate is greatest.

To study the sucrose crystals which grow out of the sugar glass plans for a home built hot stage and new procedures were developed. In order to find out where the crystals were located within the sample two techniques were developed and used. The first method was used on samples with no cover slide and utilized water to dissolve away layers of the sample. Images of the crystals were taken as the sample decreased in size. The second method was used for samples with cover slides. These samples were pried apart so some of the sample stuck to both slides and the thickness of the remaining sample was compared to the amount of crystals in the same area. Intentional scratches were also put on the surface of some of the samples using fine grit sandpaper to study the effect of surface scratches. The development of the hot stage allowed for the crystals to be observed and photographed as they were heated and grown. Refer to Appendix 1 for more on the home built hot stage.

3. Results and discussion

3.1. Maximum growth rate temperature

Sugar glasses were prepared and heated to determine the temperature at which crystallization occurs most readily. Results show that the temperature which grew the most and largest crystals was 120°C. Figures 4 shows two of the temperature versus area fraction curves which resulted from the testing. Though the levels of crystallization varied greatly, and there were occasional dips in the curve, 120°C consistently yielded the highest area fraction of crystals. This experiment, though repeatable, resulted in questions about whether it was the nucleation or growth rate that was measured.

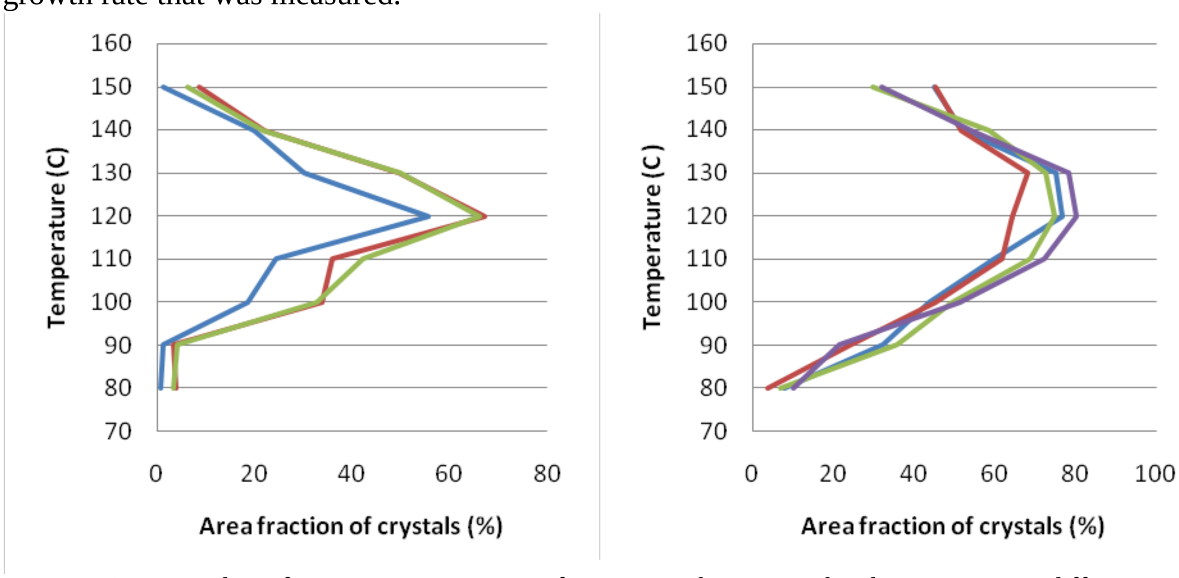


Figure 4. Plots of temperature versus area fraction. Each curve on the plots represents a different analysis of the same data. Nearly all curves peak at or around 120°C.

3.2. Crystal nucleation and growth

The home built hot stage was used to determine if 120°C represents the maximum temperature for nucleation or growth. Dozens of samples were examined at magnifications ranging from 2.5 to 10x while on the hot stage. For the majority of the samples very few, if any, small crystals were noted before heating. Within 2-3 minutes of heating, however, the crystals were visible. After this initial appearance only growth was observed. It seems that the crystal nuclei are within all of the samples when they are made and only grow large enough to see after a few minutes of heating. This observation meant that the first experiments measure the maximum temperature for crystal growth, rather than crystal nucleation.

3.3 Crystal morphology

While observing crystal growth, two or three prominent crystal morphologies were noted, none of which were characteristic of the rectangular sucrose crystals that are usually seen. These morphologies are shown in Figure 5. Prior research suggests that the different crystals morphologies form at different temperatures; however that pattern could not be seen during this research. The same research sites the corn syrup as the cause of the uncharacteristic morphologies. (Levenson, Hartel, 2004) More observation of these morphologies should be done in the future.

Figure 5. Crystal morphologies observed in sugar glass samples.

3.4. Location of crystal growth

After using the procedure previously outlined for locating crystals on many samples it was determined the crystals are growing in the bulk of the material. Though the crystal growth appears to be homogeneous, it is unlikely given that heterogeneous nucleation is much more energetically favorable. It is hypothesized that the crystals are actually forming on preexisting interfaces, whether they be tiny dust particles or bubbles, which are too small to see. Observation also found that in many samples the crystals grew in curved lines which appear to be flow lines. This may be the result of different cooling temperatures or variation in sample preparation, however further research must be done on the topic.

4. Conclusion

Studying sugar glass is an easy and affordable way to examine glass crystallization in the home laboratory. Sugar glass samples display much variation, depending on their age, environment, or batch. Though the amount of crystallization may vary, for sugar glass made with a 2:1 sugar to corn syrup dry weight ratio, the growth rate is consistently at a maximum at 120°C. The crystals appear to grow in the bulk of the material unless the surface has been scratched, intentionally or otherwise. Though many questions remain unanswered, much has been learned through studying sugar glass.

5. Acknowledgments

Support provided by the International Materials Institute for New Functionality in Glass (NSF–IMI, DMR-0409588) and the National Science Foundation

I would also like to thank my advisor, Dr. William Heffner, for his constant support, guidance, and excitement during this project.

6. References and Further Reading

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Further reading

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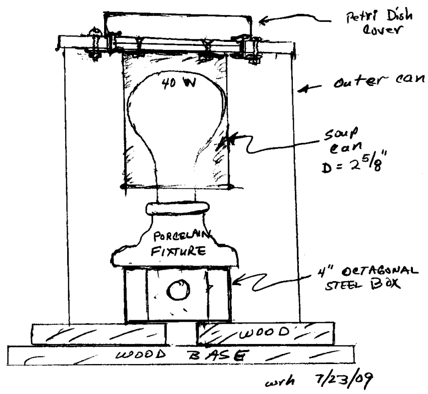
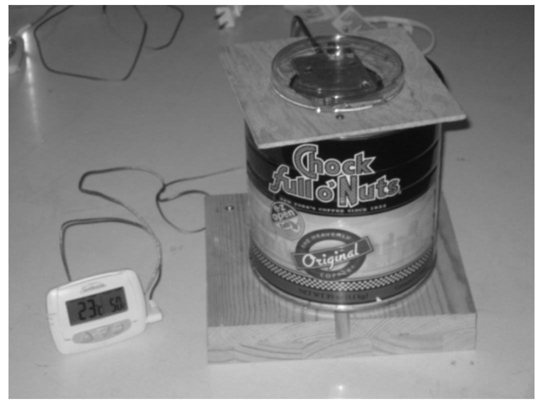
Edgar Dutra Zanotto, Federal University of Sao Carlos, Brazil
From lecture 9 of US-Japan Winter School Lectures (Kyoto, Japan, January 2008) available on International Materials Institute for Glass website at
http://www.lehigh.edu/imi/WS_Japan.htm

7. Appendices

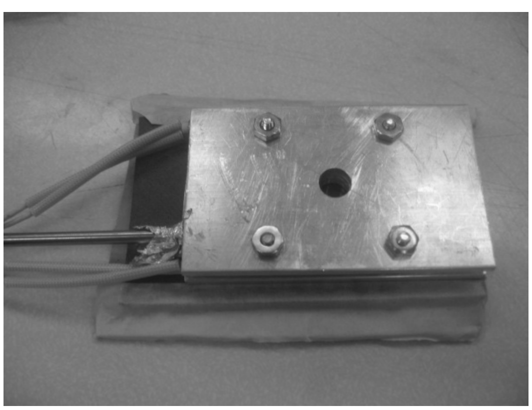
Appendix A: Equipment Design

Home-Built Sample Heater





Home-Built Hot Stage



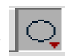
Appendix B: Image Analysis

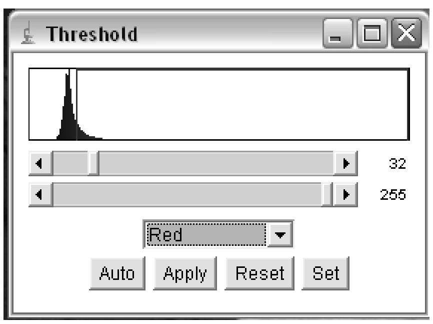
Image J Operation

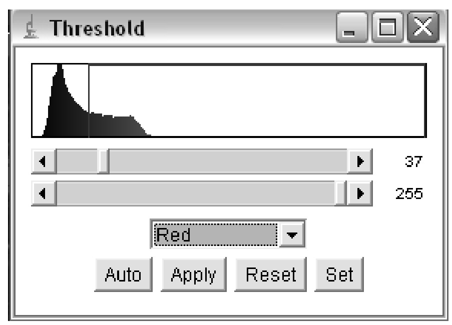
Image J is Image Processing and Analysis software that uses Java and can be downloaded for free from http://rsbweb.nih.gov/ij/.

Image J was used to calculate the area fraction of the crystals within the candy glass samples. The procedure detailed below was used.

1. Open the image. *File<Open<*find desired image

2. Outline the area for analysis. *Click elliptical selections* <Adjust ellipse to desired size
3. Change to 8-bit black and white image. *Image<Type<8-bit*
4. Enhance contract of image. *Process<Enhance contrast*
5. Adjust threshold. *Image<Adjust<Threshold*<Adjust the bottom sliding bar the whole way to the right and the top sliding bar to be half way between the beginning and the end of the black area, as shown below. This should turn all of the white crystals red.
Once it looks like the level is right to reflect the crystalline regions, select SET





6. Analyze particles. *Analyze<Set Measurements<Check area fraction<Ok<Analyze Particles…<Check display results and summary<Ok*
7. Get Area fraction: *Analyze<Measure< Ok*

For help or other information about Image J go to http://rsbweb.nih.gov/ij/docs/index.html.

http://rsbweb.nih.gov/ij/docs/pdfs/examples.pdf

S. Horst with wrh edits 9/7/11 version