

## ***Enhancement of Lithium Disilicate Microstructure Graded Glass-Ceramic***

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### ***Abstract***

*In order to advance the mechanical properties, a traditional physical growth process was useful to a lithium disilicate (LD) glass-ceramic with a dual-phase microstructure consisting of a glassy matrix and LD crystals. The main objective of this work was to make a microstructure graded glass-ceramic and examine the resulting properties as a gathering of crystallization processing. The preferred glass-ceramic was a lithium disilicate material that has a crystallization rise across the sample, leading to functionally graded properties as a effect of the microstructure rise . Samples were prepared by melting and bucketing glass at 1400°C, annealing at 410°C for 48 hours, and nucleating at 470°C for 2 hours. To ensure that crystallization would not occur homogeneously throughout the sample, a temperature rise was imposed during crystallization. Samples were crystallized on a self-constructed resistance wire furnace that was open to air. Several crystallization processing parameters were tested, including high temperature for a short time and low temperature for a long time. Samples were ground and polished to 0.25 microns before categorization methods were performed. Raman spectroscopy showed a transformation of the characteristic spectra across the sample cross section, with defined, high-intensity peaks on the crystalline side and broad, low-intensity peaks on the glassy side. Micro-hardness showed a slight transition in hardness values across the sample cross section, however the unevenness was too large to draw any conclusions. The description*

*methods showed that the preferred material was formed and the ensuing properties were a gathering of the crystallization processing parameters.*

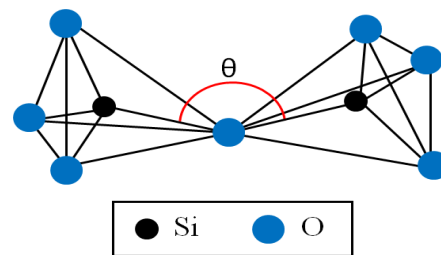
**Keywords:** - *Crystallization, Lithium disilicate glass-ceramic, temperature rise, microstructure graded material, functionally graded material*

## INTRODUCTION

Glass-ceramics are polycrystalline materials formed from special glasses [1]. A glass is first created and then transformed into a polycrystalline material through a heat treatment. This heat treatment includes controlled nucleation and crystal growth [1]. Glasses are amorphous in nature, meaning they lack long-range order [2]. In contrast, crystalline materials contain long range order [3]. To describe this further, first consider two simple materials: vitreous silica and crystalline silica. Both materials are identical in composition ( $\text{SiO}_2$ ), but differ in structure.

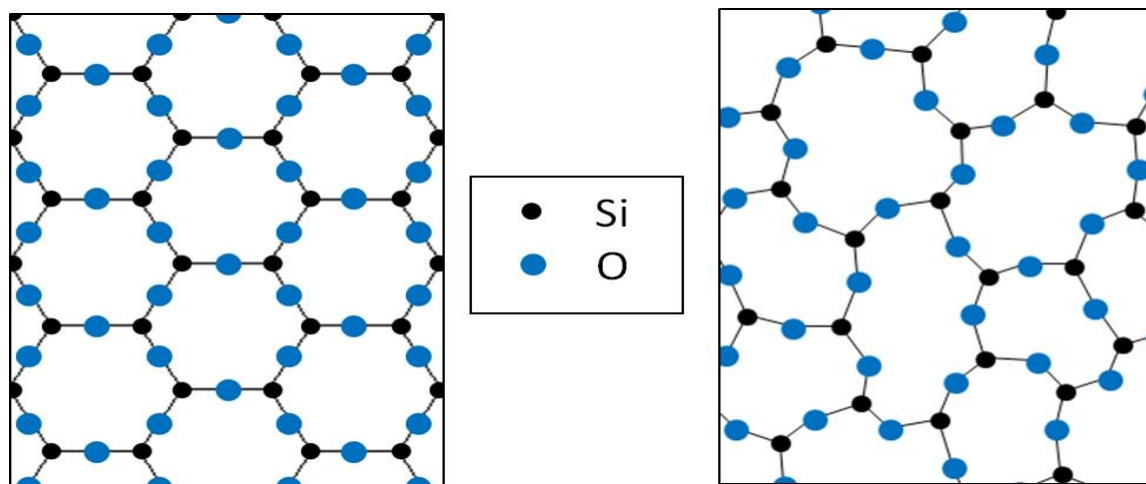
Vitreous silica is the glassy phase of silica [2]. In this phase, the material lacks long range order, but exhibits short range order. This means that the basic building block of the glass, the silica tetrahedron, is the same throughout the glassy structure. The angle of the bond inside the tetrahedron, the O-Si-O bond, will remain constant. However, the connections of numerous tetrahedrons can vary. The angle of the bond

connecting two tetrahedrons, the Si-O-Si bond, can vary between  $140^\circ$  and  $180^\circ$  in vitreous silica [2]. A representation of the Si-O-Si bond angle can be seen in the figure below.



**Figure 1: 2 silica tetrahedrons with the Si-O-Si bond angle shown in red.**

On another hand, crystalline materials hold long range order [3]. This means that in crystalline silica (quartz), the Si-O-Si bond angle will be the same during the material. The figure below is a diagram that shows the presence of long range order in crystalline silica and the lack of long range order in vitreous silica. Note that in the figure below, the fourth oxygen atom in the tetrahedron is not depicted. In reality, this oxygen would be directly above or below the pictured silicon.

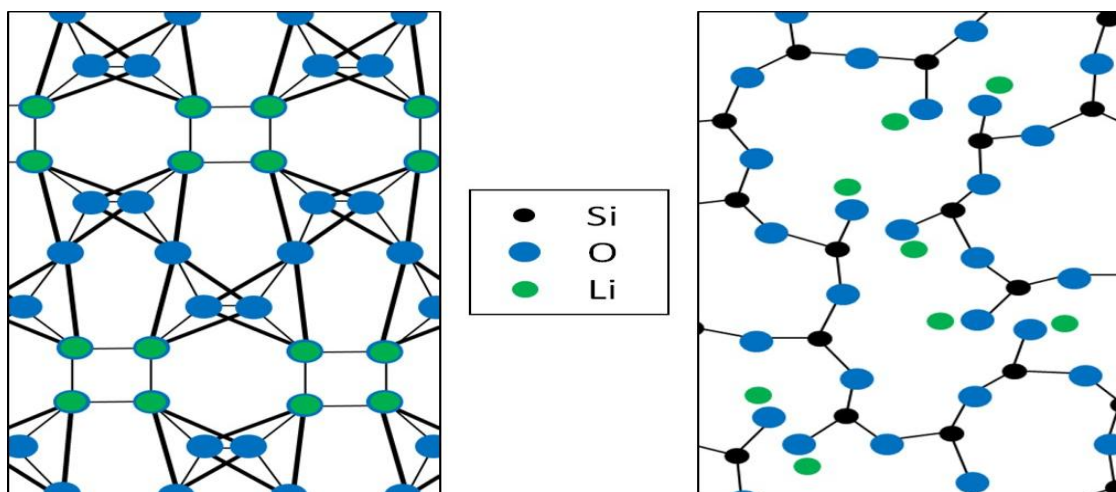


*Figure 2: 2D representation of the structure of silica crystals (left) and glasses*

Now consider a more complicated material system: lithium disilicate. Lithium disilicate glass has two components [2]. The first is silica, which serves as the glass former. The glass former is the most abundant material and is the primary source of structure. The second is lithium oxide ( $\text{Li}_2\text{O}$ ), which serves as the flux. The purpose of the flux is to lower the processing temperature of the glassformer. In this case, the addition of lithium oxide reduces the processing temperature of the glass from approximately  $2000^\circ\text{C}$  to  $1100^\circ\text{C}$  [2].

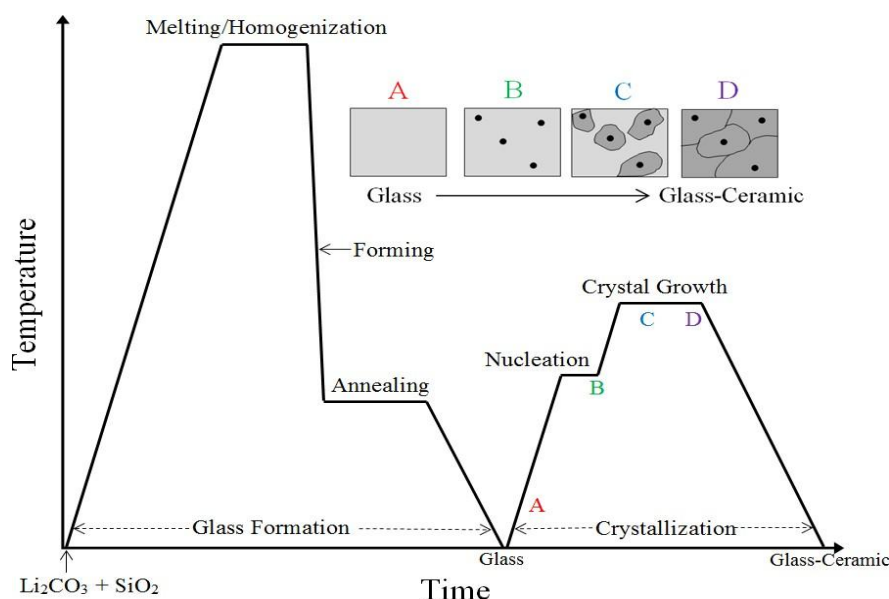
Since silica is the glassformer, the structure of lithium disilicate glass largely resembles the structure of vitreous silica.

However, the addition of lithium oxide to silica alters the glass structure slightly [2]. Lithium oxide will infiltrate the structure near an oxygen atom. The addition of the lithium oxide will break one of the Si-O bonds to that oxygen atom, and the lithium oxide will split into two ions ( $\text{LiO}^-$  and  $\text{Li}^+$ ). The  $\text{Li}^+$  ion will bond with the existing oxygen atom (now with only one Si-O bond), and the  $\text{LiO}^-$  ion will bond with the other silicon atom (now missing an oxygen). The resulting structure will be two oxygen atoms where there used to be one, with two lithium atoms connection nearby. The addition of lithium oxide causes non-connection oxygens to form. These non-connection oxygens are oxygen atoms that only have one Si-O connection [2].



**Figure 3: 2D representation of the arrangement of lithium disilicate crystals (left) and glasses (right).**

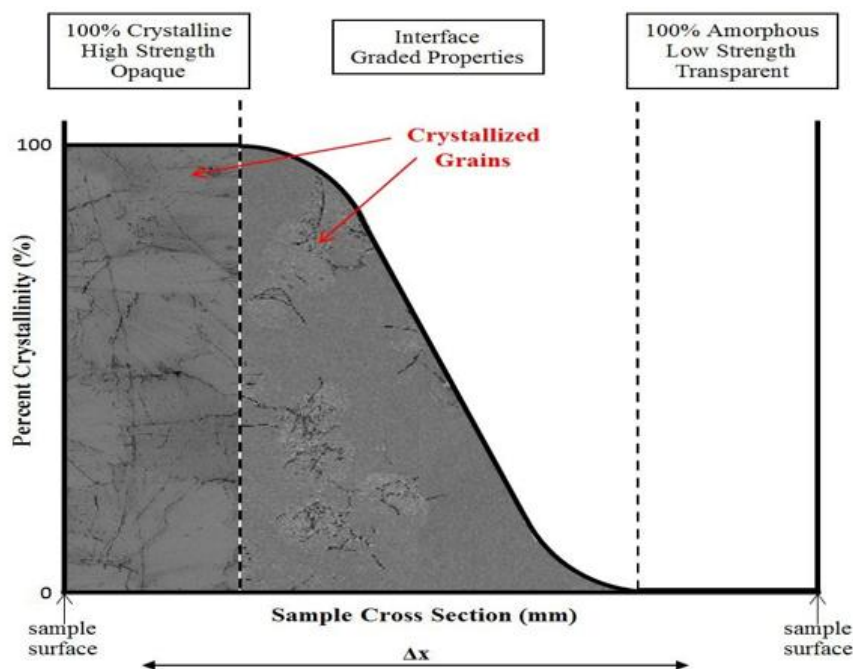
In the design of a lithium disilicate glass-ceramic, the arrangement of the material would convert from the glassy phase to the crystalline phase. However, glass-ceramics are polycrystalline materials, meaning they contain not one crystal, but various crystals filled together (3). These crystals are known grains and can be in many different crystallographic orientations. While short range order exists throughout the material, long variety order only exists throughout individual grains. A typical heating curve for the creation of a glass-ceramic can be shown below.



**Figure 3: Characteristic thermal history for the formation of a glass-ceramic.**

Glass-ceramics are used in several applications ranging from stovetops to dental prosthetics. The major advantage of these materials is that they can be simply formed in the glassy state and then distorted into a partly or entirely crystalline state. Properties of the resulting glass-ceramic vary significantly depending on the percent crystallization. For example, in the glassy state, the material will appear optically transparent and exhibit only a moderate value of strength. By partially crystallizing, the strength of the material will increase and it will become translucent. When fully crystallized, the material will exhibit high strength and become opaque.

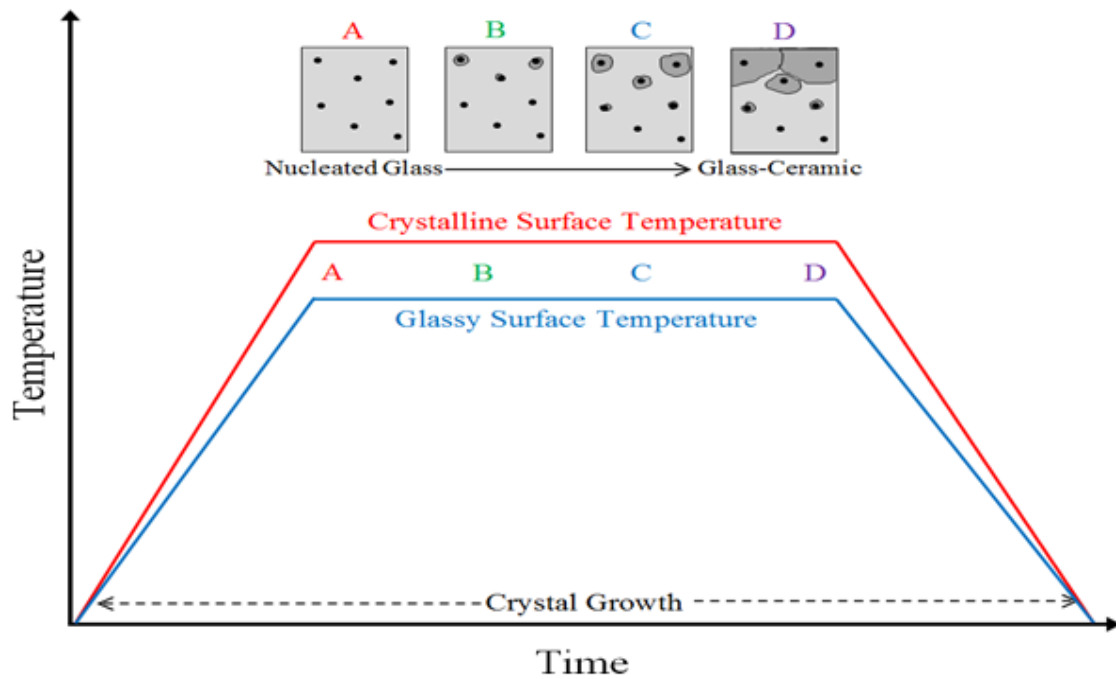
In addition to the sum of crystallization, the range of crystals current can involve the material properties. Together the crystal range and level of crystallization are restricted by the processing time and temperature [2]. A thin population of nuclei but wide crystal expansion will result in fewer, superior crystals present in the material. An plentiful population of nuclei and small crystal growth will result in numerous, smaller crystals present in the material. Furthermore, the rate at which nucleation and crystallization occur is controlled by the temperature of the heat treatment. Below is a graph that shows the dependency of nucleation and crystallization rates on temperature.



**Figure 5: Graph of percent crystalline Vs the sample cross section for a microstructure graded material with a steep interface.**

To produce surroundings in which crystallization would happen on one surface but not regularly throughout the sample, a distinctive processing method is needed. The processing method that was chosen for this experimentation was a temperature rise forced during crystallization. If a temperature rise is imposed across a homogeneously nucleated sample such that temperatures

required to initiate crystallization are current at one surface, but not at the reverse surface, a crystallization rise is possible. This can be as shown in below diagram. This study will detail the process developed that involves a temperature rise imposed across a sample during crystallization to create a microstructure graded glass-ceramic.



**Figure 6: Representation of the creation of a microstructure graded glass-ceramic by imposing a temperature difference across the sample during crystallization.**

**EQUIPMENT AND EXPERIMENTAL PROCEDURE:**

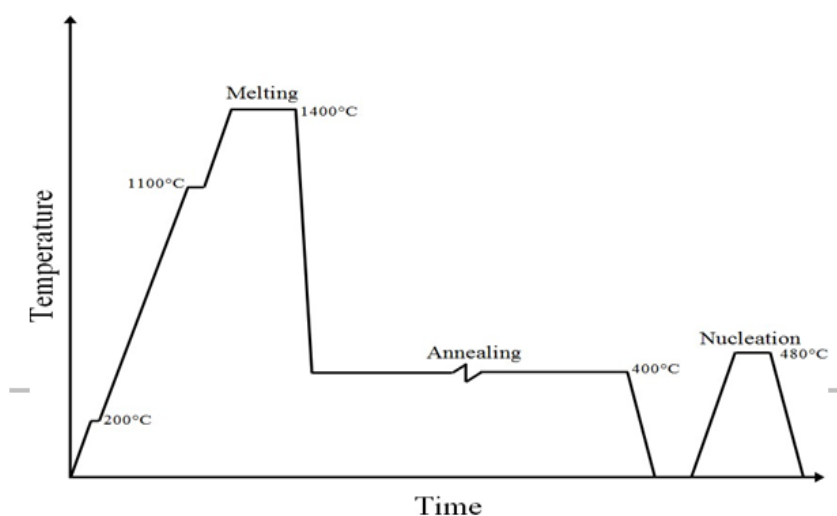
This part information the procedure and experimental parameters for the incomplete crystallization of lithium disilicate glass into a glass-ceramic. Glass preparation, crystallization, characterization methods, and change in material properties are described below.

This melting cycle was broken up into three components:

- The temperature was raised slowly to 200°C and held there for 30 minutes to remove any moisture from the frit.
- The temperature was then raised slowly to 1100°C and held there for one hour to create a congruent melt.
- The temperature was then raised slowly to 1400°C and held there for four hours to create a low viscosity

melt so that the melt could be easily poured into a mold.

The glass melt was cast into a hot graphite mold (400°C) to create rods (60 mm long, 15 mm diameter), and samples were rapidly transferred into a box furnace (Thermolyne- Model 1400) at 400°C for 48 hours. This last step was used to anneal the samples and remove the stress and strain present inside the rods. After annealing, the samples were allowed to furnace cool to room temperature. The glass samples were then heated in an electric furnace (CM furnace-Model 1700) at 480°C for 2 hours to initiate nucleation, and then allowed to furnace cool to room temperature. Shown in the figure below is the entire heating process to prepare the nucleated glass.



**Figure 7: Heating condition for the making and nucleation of the glass. Note that there is a break shown in the graph during annealing.**

Crystallization heating profiles for all the samples can be seen in the following diagrams. In the diagrams below, the red line reports the temperature recorded by Thermocouple 1, the temperature at the crystalline surface. The blue line reports

the temperature recorded by Thermocouple 2, the temperature at the glassy surface. Note that for Samples 7, 8, 10, and 11, the cooling rate was controlled by the furnace.

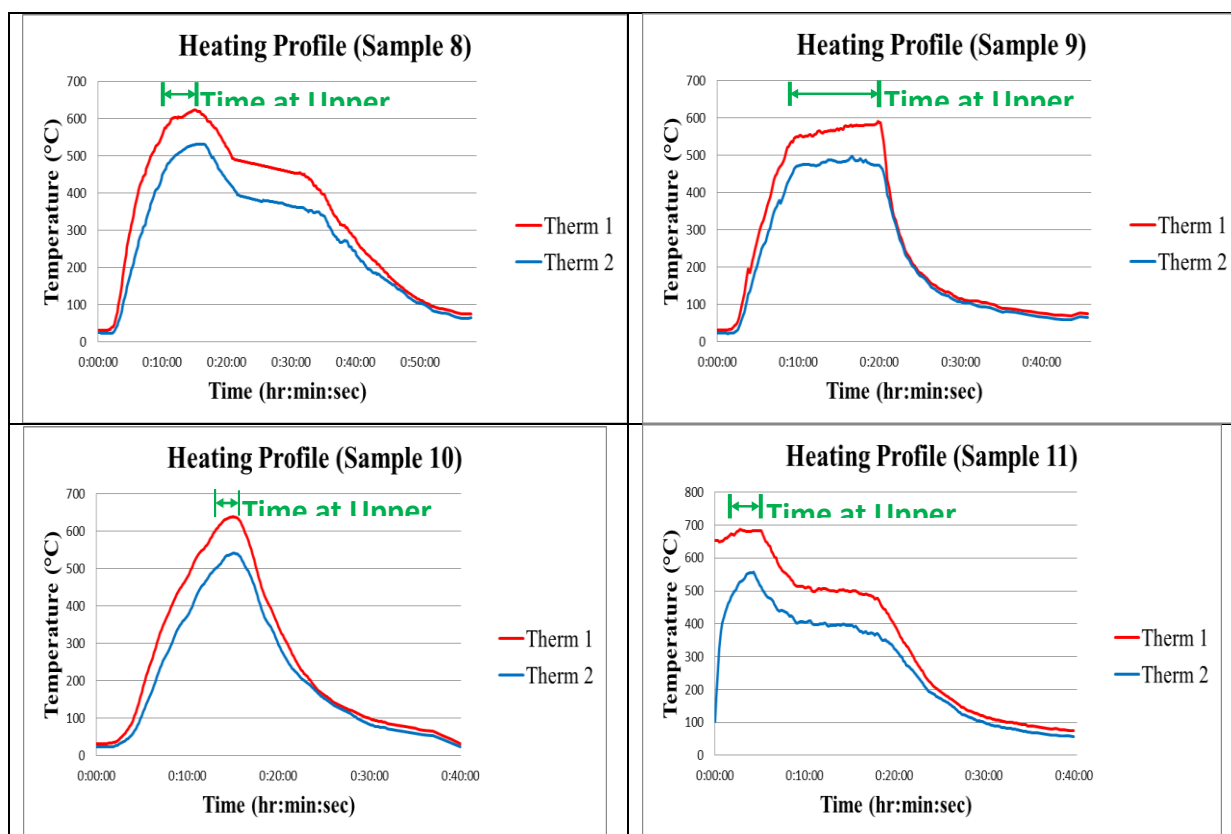


Figure 8: Crystallization heating profile for Sample 8, 9, 10 and 11

Literature standards of density, coefficient of thermal expansion, modulus of elasticity, and hardness for lithium disilicate glass and glass-ceramic.

Material	True Density (g/cm <sup>3</sup> )	Thermal Expansion Coefficient (10 <sup>-5</sup> °C <sup>-1</sup> )	Modulus of Elasticity (GPa)	Vickers Hardness (kg/mm <sup>2</sup> )
Lithium Disilicate -Glass	2.348	3.4	86	530
Lithium Disilicate Glass-Ceramic	2.437	1.23	93	540



Function of the Rule of Mixtures can predict the density, coefficient of thermal expansion, modulus of elasticity, and hardness for a partially crystallized material. The use of Equation 2 would yield the values reported in Table 2.

Application of the Rule of Mixtures to the true density, coefficient of thermal expansion, modulus of elasticity, and hardness for partially crystallized lithium disilicate.

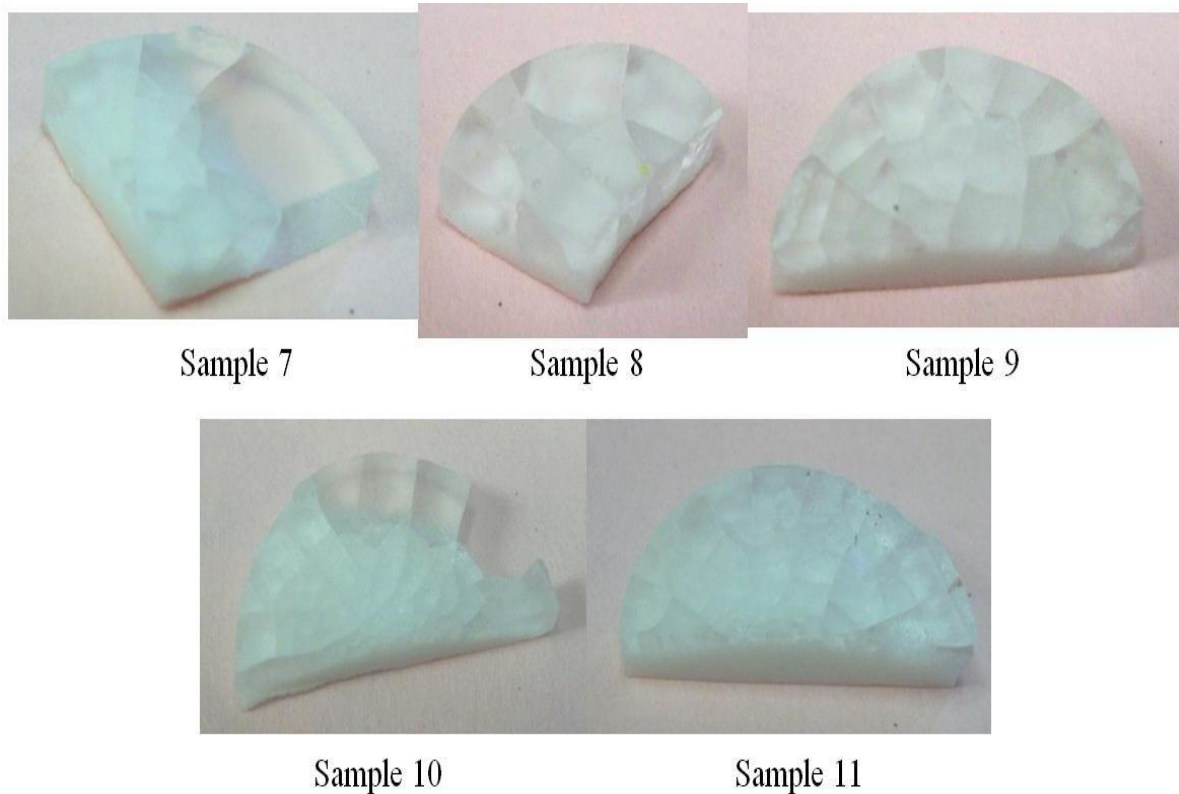
Crystallinity (%)	True Density (g/cm <sup>3</sup> )	Thermal Expansion Coefficient (10 <sup>-5</sup> °C <sup>-1</sup> )	Modulus of Elasticity (GPa)	Vickers Hardness (kg/mm <sup>2</sup> )
0	2.348 (m)	3.40 (m)	86 (m)	530 (m)
20	2.366 (c)	2.97 (c)	87 (c)	532 (c)
40	2.384 (c)	2.53 (c)	89 (c)	534 (c)
60	2.401 (c)	2.10 (c)	90 (c)	536 (c)
80	2.419 (c)	1.66 (c)	91 (c)	538 (c)
100	2.437 (m)	1.23 (m)	93 (m)	540 (m)

It is important to be able to approximate the intermediate properties in a functionally graded material to understand the behavior at the graded interface.

**RESULTS AND DISCUSSION:**

The first result from this experiment was the creation of a microstructure graded glass-ceramic. The desired material was prepared using the procedures described above. Examples of these samples can be

seen in the figure below. Note that in some samples, the amount of crystallization is not constant throughout the cross section (i.e. there is more crystallization in the center of the sample than closer to the outside). Throughout this work , the samples were analyzed as close to the center of the sample as possible.



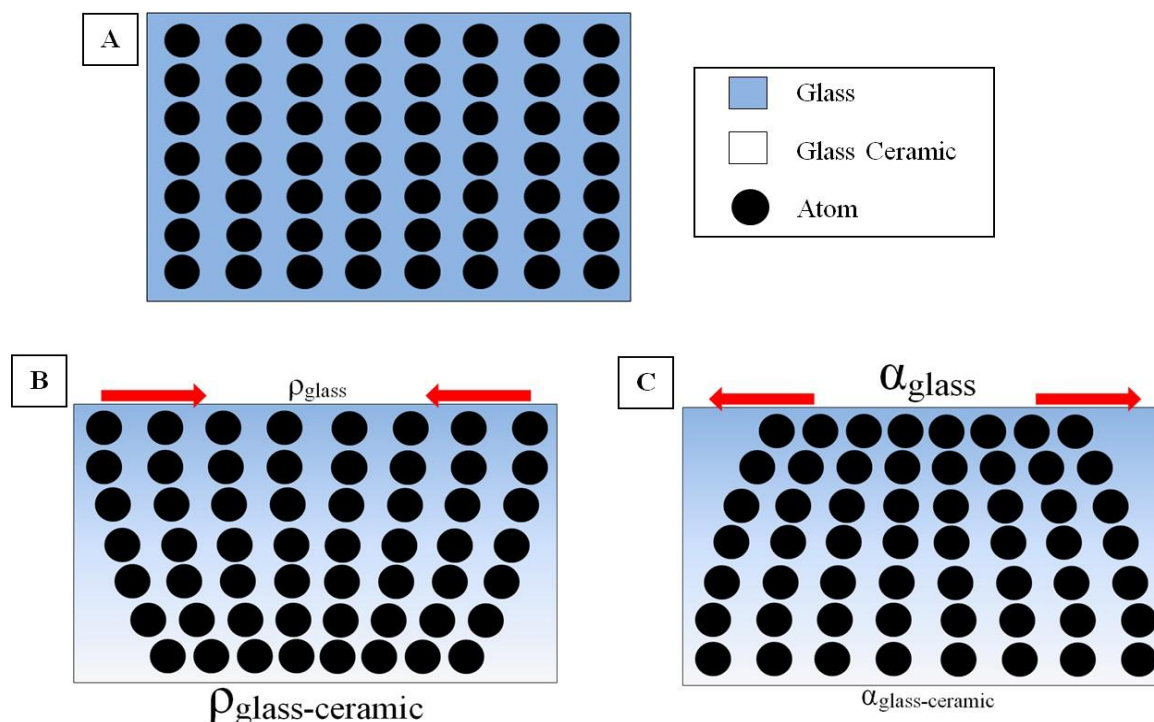
**Fig 9: Pictures of Samples 7-11 looking at cracks in the smooth stage.**

Pictures of microstructure graded samples. A) View looking at the crystallized surface of Sample 9. B) View looking at the cross section of Sample 7 with the crystallized region to the left. C) View looking at the glassy surface of Sample 9. As can be seen in the figure above, cracks occurred throughout the glassy portion of the material. The figure below shows pictures of each sample looking at the glassy surface.

The fast in the glassy phase is believed to be due to dissimilar properties in the glass and glass-ceramic, resulting in stress. Cracking will occur when the stress is

larger than the fracture stress of either the glass or the glass-ceramic. The fracture stress of glass is about 64 MPa, and for the glass-ceramic is about 215 MPa [12].

The density of the glass is 2.348 g/cm<sup>3</sup>, and the density of the glass-ceramic is 2.437 g/cm<sup>3</sup>. The density of the glass-ceramic is greater than the density of the glass. The coefficient of thermal expansion of the glass is  $3.4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ , and the coefficient of thermal expansion of the glass-ceramic is  $1.23 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ . The coefficient of thermal expansion of the glass is larger than the coefficient of thermal expansion of the glass-ceramic.



**Fig 10: detailed awarding stresses imposed on glass surface due to difference in material properties. A) Demonstration of glass exclusive of stresses. B) Demonstration of compression on glass surface due to densification of crystalline segment. C) Demonstration of tension on glass surface due to thermal shrinkage of smooth phase.**

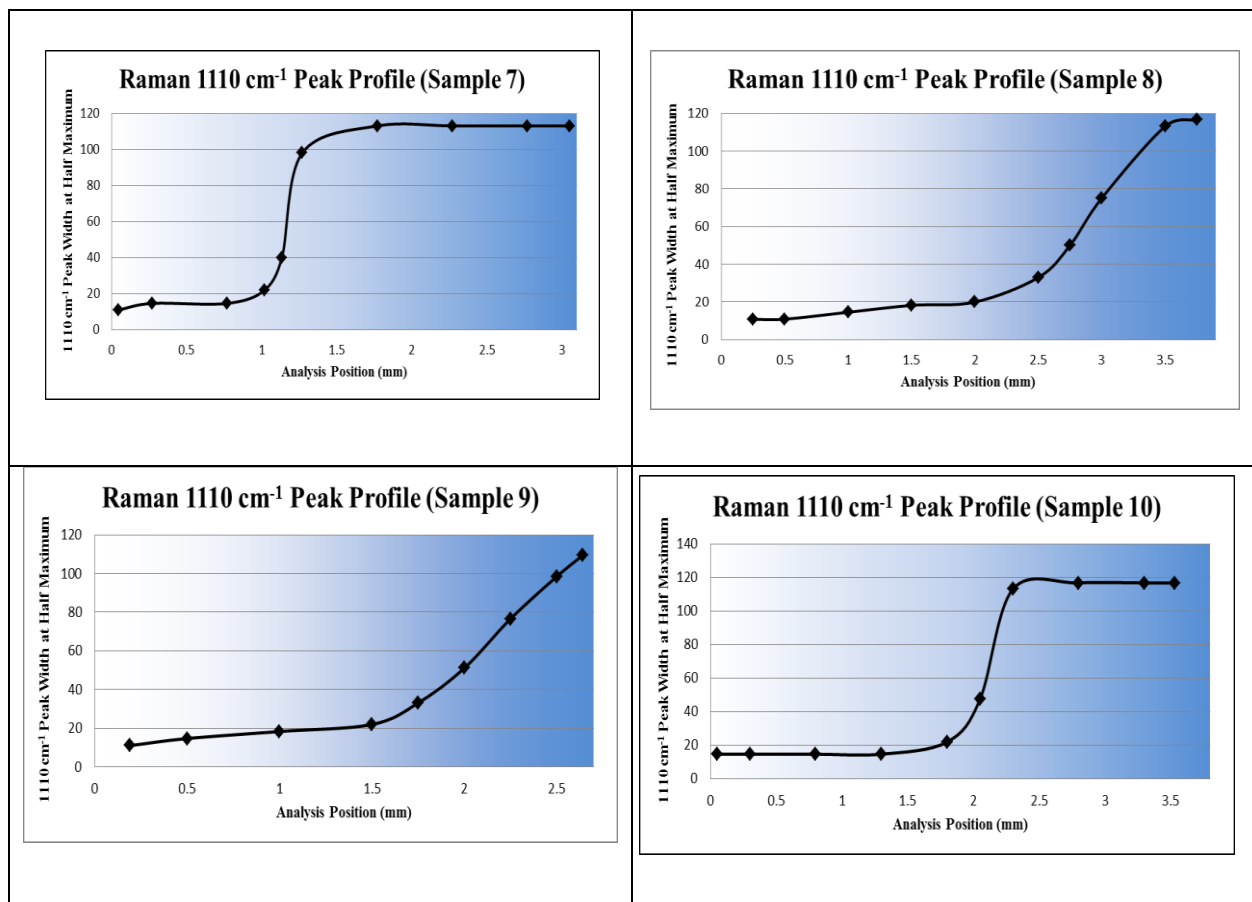
The diagram shows representations of these two material properties and the stresses they impose on the graded material. In part A of the figure, a representation is shown of a glass with atoms. This part of the figure is used as a reference of the ideal stress-free state.

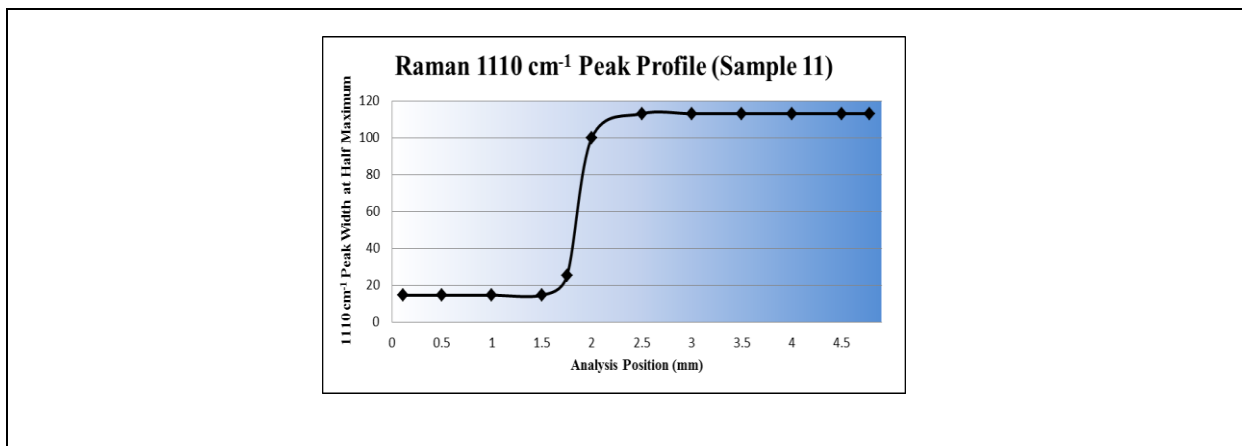
Part B of the figure shows the result of a higher density in the crystalline phase. When the nucleated glass is heated to the crystallization temperature, crystallization occurs. Since the density is higher in the crystalline phase than in the glassy phase,

this crystallization is also accompanied by densification. However, when this densification is only happening at one surface due to the temperature rise, the densification occurring at this surface will pull the opposite surface into compression. Since this densification is occurring at well above the annealing temperature of the glass, most of these stresses can likely relax out of the material. Furthermore, compression on the glassy surface tends to close cracks, not open them.

Part C of the figure shows the result of a higher coefficient of thermal expansion in the glassy phase. After the sample has been crystallized and is cooling to room temperature, the sample will shrink, as governed by the coefficient of thermal expansion. However, when there are two different phases present, each material will try to shrink a different amount. Since the glass has a higher coefficient of thermal

expansion, it will try to shrink more than the glass-ceramic during cooling. However, the glass-ceramic will oppose this shrinkage and not allow the glassy phase to shrink as much as is thermodynamically stable. This will pull the glassy phase into tension. The difference in coefficient of thermal expansion is likely the cause of the cracking observed in the study.





*Figure 11: Graph of Raman spectra 1086-1110 cm-1 peak width across Sample 7, 8, 9, 10 & 11.*

#### SUMMARY AND CONCLUSIONS

- A linear rise resistance wire furnace was designed and constructed.
- Application of a temperature rise imposed across a sample during crystallization resulted in a lithium disilicate microstructure graded glass-ceramic.
- Different crystallization heating parameters resulted in unstable crystallinity rises.
- High temperature, moderate temperature rise, and short time resulted in a steep crystallization rise.
- Low temperature, high temperature rise, and a long time resulted in a shallow crystallization rise.

Preferential crystallization as a means to create a microstructure graded material provided a useful method for controlling properties without altering the chemical composition. If work were to continue on this topic to produce a crack free material, microstructure graded glass-ceramics could be functional in a lot of potential applications. With more sophisticated processing equipment, parameters could be controlled to create a wide range of functionally graded materials.

Prospect Work: This experiment has proven that it is possible to create a

microstructure graded glass-ceramic by imposing a temperature rise across the material during crystallization. However, there are many areas of work that could expand on this topic.

The most obvious is the bulk creation of a microstructure graded glass-ceramic without resulting in cracking through the glassy phase. Further exploration could develop the experimental parameters necessary to create a stress-free material. possibly a temperature rise furnace could be used to more precisely control the temperature rise during crystallization. The temperature rise directly controls the resulting crystallization rise . There could be a crystallization rise , and therefore a thermal expansion rise , that would result in a gradual enough change that would not cause cracks upon cooling.

## REFERENCES

- I. E.D. Zanotto, A bright future for glass-ceramics, *Am. Ceram. Soc. Bull.* 89 (2010) 19–27.
- II. F.C. Serbena, E.D. Zanotto, Internal residual stresses in glass-ceramics: a review, *J. Non-Cryst. Solids* 358 (2012) 975–984.
- III. M. Dittmer, C. Ritzberger, M. Schweiger, V. Rheinberger, M. Wörle, W. Höland, Phase and microstructure formation and their influence on the strength of two types of glass-ceramics, *J. Non-Cryst. Solids* 384 (2014) 55–60.
- IV. M. Bengisu, R.K. Brow, J.E. White, Interfacial reactions between lithium silicate glass-ceramics and Ni-based superalloys and the effect of heat treatment at elevated temperatures, *J. Mater. Sci.* 39 (2004) 605–618.
- V. W. Höland, V. Rheinberger, E. Apel, C. van't Hoen, Principles and phenomena of bioengineering with glass-ceramics for dental restoration, *J. Eur. Ceram. Soc.* 27 (2007) 1521–1526.
- VI. F.C. Serbena, I. Mathias, C.E. Foerster, E.D. Zanotto, Crystallization toughening of a model glass-ceramic, *Acta Mater.* 86 (2015) 216–228.
- VII. A. Koike, S. Akiba, T. Sakagami, K. Hayashi, S. Ito, Difference of cracking behavior due to Vickers

- indentation between physically and chemically tempered glasses, *J. Non-Cryst. Solids* 358 (2012) 3438–3444.
- VIII. İ. Erdem, D. Guldiren, S. Aydin, Chemical tempering of soda lime silicate glasses by ion exchange process for the improvement of surface and bulk mechanical strength, *J. Non-Cryst. Solids* 473 (2017) 170–178.
- IX. H. Fischer, H.R. Maier, R. Marx, Improved reliability of leucite reinforced glass by ion exchange, *Dent. Mater.* 16 (2000) 120–128.
- X. H. Fischer, R.A. De Souza, A.M. Wätjen, S. Richter, D. Edelhoff, J. Mayer, M. Martin,
- XI. R. Telle, Chemical strengthening of a dental lithium disilicate glass–ceramic material, *J. Biomed. Mater. Res.* 87A (2008) 582–587.
- XII. K. Łączka, K. Cholewa-Kowalska, M. Środa, J. Rysz, M.M. Marzec, M. Łączka, Glass–ceramics of LAS (Li<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>) system enhanced by ion-exchange in KNO<sub>3</sub> salt bath, *J. Non-Cryst. Solids* 428 (2015) 90–97.
- XIII. C. Guillemet, Annealing and tempering of glass, *J. Non-Cryst. Solids* 123 (1990) 415–426.
- XIV. B.W. Fan, K.Q. Zhu, Q. Shi, T. Sun, N.Y. Yuan, J.N. Ding, Effect of glass thickness on temperature gradient and stress distribution during glass tempering, *J. Non-Cryst. Solids* 437 (2016) 72–79.
- XV. F. Petit, A.C. Sartieaux, M. Gonon, F. Cambier, Fracture toughness and residual stress measurements in tempered glass by Hertzian indentation, *Acta Mater.* 55
- XVI. Shelby, J. E. (2005). Introduction to glass science and technology. (2 ed.). Cambridge, UK: The Royal Society of Chemistry.
- XVII. Kingery, W. D., Bowen, H. K., & Uhlmann, D. R. (1975). Introduction to ceramics. (2 ed.). New York, NY: John Wiley & Sons.
- XVIII. Fang, L., Gao, Y., & Zhang, Z. (1999). Tribology of si<sub>3</sub>n<sub>4</sub> with different glassy phase content sliding against grey cast iron lubricated with water. *Wear*,

- 225(2), 896-904. Retrieved from <http://www.sciencedirect.com/science/article/pii/S0043164898004086>
- XIX. Neubrand, A. (2001). Functionally Graded Materials. *Encyclopedia of Materials - Science and Technology* (p. 3407-3413). Elsevier. Retrieved May 2, 2012, from [http://www.knovel.com.ezproxy.lib.vt.edu:8080/web/portal/browse/display?\\_EXT\\_KNOVEL\\_DISPLAY\\_bookid=1871&VerticalID=0](http://www.knovel.com.ezproxy.lib.vt.edu:8080/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=1871&VerticalID=0)
- XX. Tilley, R. (2000). "Colour and the optical properties of materials." (pp. 151-155). West Sussex, England: John Wiley & Sons.
- XXI. Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>, 1997-2011.
- XXII. Vander, G. F. (2000). Microindentation hardness testing. In H. Kuhn & D. Medlin (Eds.), *ASM Handbook, Volume 8: Mechanical Testing and Evaluation* (pp. 221-231). ASM International.
- XXIII. Buchner, S., Lepienski, C. M., Soares Jr., P. C., & Balzaretto, N. M. (2011). Effect of high pressure on the mechanical properties of lithium disilicate glass ceramic. *Materials Science and Engineering*, (528), 3921-3924. Retrieved from <http://www.sciencedirect.com/science/article/pii/S0921509311001171>
- XXIV. Yamane, M., & Mackenzie, J. D. (1974). Vicker's hardness of glass. *Journal of Non-Crystalline Solids*, 15, 153-164. Retrieved from <http://www.sciencedirect.com/science/article/pii/0022309374900441>
- XXV. Albakry, M., Guazzato, M., & Swain, M. V. (2003). Fracture toughness and hardness evaluation of three pressable all-ceramic dental materials. *Journal of Dentistry*, 31, 181-188. Retrieved from <http://www.sciencedirect.com/science/article/pii/S0300571203000253>



- XXVI. Bona, A. D., Mecholsky, J. J., & Anusavice, K. J. (2004). Fracture behavior of lithia disilicate- and lucite-based ceramics. *Dental Materials*, 20(10), 956-962. Retrieved from <http://www.sciencedirect.com/science/article/pii/S01095641040>