MECHANISMS FOR THE CRYSTALLIZATION OF ZBLAN

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Abstract

The objective of this ground based study is to test the hypothesis that shear thinning (the non-Newtonian response of viscosity to shear rate) is a viable mechanism to explain the observation of enhanced glass formation in numerous low-g experiments. In 1-g, fluid motion results from buoyancy forces and surface tension driven convection. This fluid flow will introduce shear in undercooled liquids in 1-g. In low-g it is known that fluid flows are greatly reduced so that the shear rate in fluids can be extremely low. It is believed that some fluids may have weak structure in the absence of flow. Very small shear rates could cause this structure to collapse in response to shear resulting in a lowering of the viscosity of the fluid. The hypothesis of this research is that:

Shear thinning in undercooled liquids decreases the viscosity, increasing the rate of nucleation and crystallization of glass forming melts. Shear in the melt can be reduced in low-g, thus enhancing undercooling and glass formation.

The viscosity of a model glass (lithium di-silicate, L2S) often used for crystallization studies has been measured at very low shear rates using a dynamic mechanical thermal analyzer. Our results are consistent with increasing viscosity with a lowering of shear rates. The viscosity of L2S may vary as much as an order of magnitude depending on the shear rate in the temperature region of maximum nucleation and crystal growth. Classical equations for nucleation and crystal growth rates, are inversely related to the viscosity and viscosity to the third power respectively. An order of magnitude variation in viscosity (with shear) at a given temperature would have dramatic effects on glass crystallization

Crystallization studies with the heavy metal fluoride glass ZBLAN (ZrF_2-BaF_2-LaF_3-AlF_3-NaF) to examine the effect of shear on crystallization are being initiated. Samples are to be melted and quenched under quiescent conditions at different shear rates to determine the effect on crystallization.

The results from this study are expected to advance the current scientific understanding of glass formation in low-g and glass crystallization under glass molding conditions and will improve the scientific understanding of technological processes such as fiber pulling, bulk amorphous alloys, and glass fabrication processes.

Introduction

The heavy metal fluoride glasses represent a class of reasonably good glass forming compositions with very unique infrared optical properties that have been of interest to researchers for 20 years.[1] The most extensively studied glass with the most potential for practical applications is ZBLAN, which contains

Keywords: shear thinning, glass, ZBLAN, glass formation, low gravity, new research

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the fluorides of zirconium, barium, lanthanum, aluminum, and sodium. It has a broad transmission range (0.3-6μm), low index of refraction (~1.43), low dispersion, low Raleigh scattering, ultra-low thermal dispersion, and potential ultra-low signal attenuation[2]. Potential applications include fiber amplifiers, fiber optic gyroscopes, delivery systems for laser cutting, drilling and surgery, radiation resistant data links, nonlinear optical systems, and ultra-low-loss repeater-less transcontinental and transoceanic optical fiber. Potential markets for these materials are in the tens of billions of dollars per year[3].

Optical fiber from this material has excellent transmission characteristics in the IR, but the glass is somewhat susceptible to nucleation and crystallization. The theoretical intrinsic loss coefficient for ZBLAN at 2 microns is 0.001 dB/Km. Extrinsic losses, however, cause significant attenuation. The lowest loss coefficient measured is 0.7 dB/Km. This compares with the loss coefficient for fiber optic grade fused silica glass of 0.2 dB/Km. The extrinsic losses in ZBLAN have been attributed to 1) impurities which might be lowered by containerless processing and 2) to scattering from micro-crystallites that form during glass preform production or during fiber drawing. Finding a way to better control and eliminate these nuclei could have a very significant impact on the billion dollar information fiber optic industry.

A number of experiments have been performed with glass forming materials in space that provide evidence of enhanced glass formation for glasses prepared in space. These experiments have been of two types, crystallization studies and diffusion studies.

In general, the glasses have been shown to have much more homogeneous compositional distribution[4] than terrestrial samples and the glasses have been shown to be more resistant to crystallization[5,6].

Two groups have reported that the crystallization of ZBLAN is reduced by processing in low-g[2,7]. The ZBLAN fiber in the figure on the left of Figure 1, was heat treated on Conquest-1 sub-orbital rocket flight. Its glassy nature is indicated by the smooth surface (a line of bubbles formed where it contacted the container). By contrast, the ZBLAN fiber on the right of Figure 1 was heated on Earth under identical conditions, showing a great deal of crystallization.

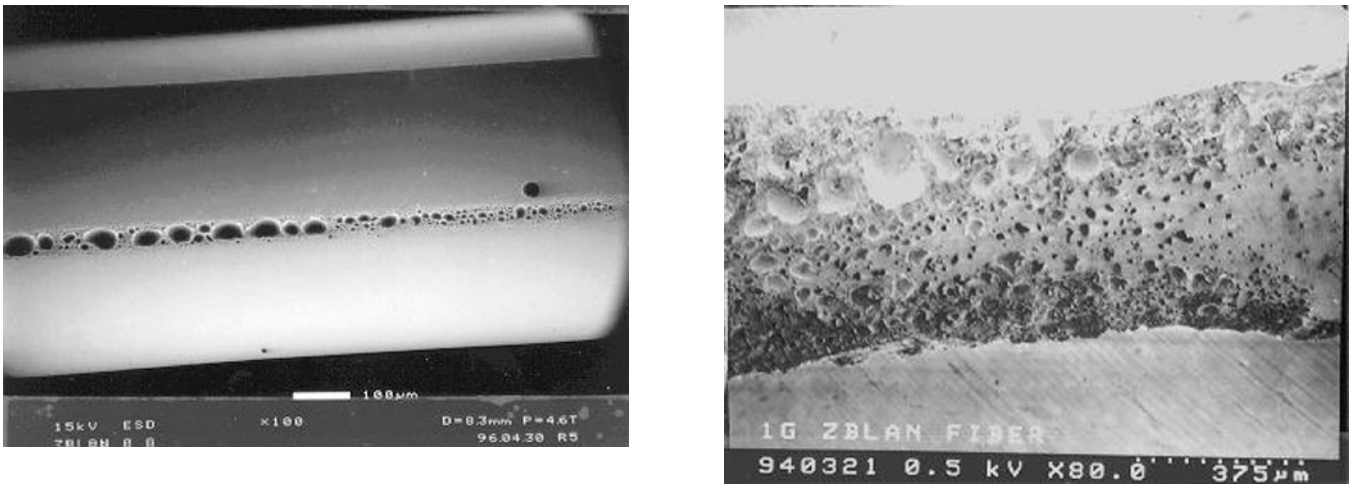

Figure 1. On left, ZBLAN fiber heated in a low-g rocket experiment with essentially no crystallization. On the right, ZBLAN fiber heated in 1-g with excessive crystallization.

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Theory

Shear Thinning is the reduction of viscosity when a fluid flows. Fluids exhibit much lower flow rates in low-g than in 1-g. If the glass exhibits shear thinning, then the viscosity will be higher in low-g than in 1-g. One can predict the effect of shear thinning on crystallization.[8] Viscosity is the only directly measurable kinetic parameter used in crystal nucleation and growth equations. In the classical treatment of crystallization[9] nucleation rate, I, and crystal growth rate, U, are both inversely proportional to viscosity, η, with the viscosity term appearing in the pre-exponential factor.

$$I = (k_n/\eta) \exp[-b\alpha^3\beta T_m/T(1-T_r)^2]$$
$$U = (k'_n/\eta) [1-\exp(-\beta(T_m-T/T)]$$

Where T_m is the melting temperature, T is the absolute temperature, and T_r is the reduced temperature. The kinetic constants k_n and k'_n, shape factor, b, and dimensionless parameters related to the liquid-crystal interfacial tension, α, and entropy of fusion, b[9].

The fraction of glass crystallized, X, with time at a given temperature[10] is a function of the rate of nucleation, the third power of the growth rate, and the fourth power of time.

$$X = (\pi/3)(IU^3t^4)$$

Under conditions of shear thinning, the effective viscosity decreases with increasing shear rate so that the viscosity can be expressed as a function of shear rate, $\eta(\varepsilon)$. The crystallization parameters such as the nucleation rate will also be a function of shear rate.

$$I(\varepsilon) = (k_n/\eta(\varepsilon))\exp[-b\alpha^3\beta T_m/T(1-T_r)2]$$

Low g-processing is known to greatly reduce convection, which reduces shear in the liquid. This would reduce any shear thinning in the liquid subsequently increasing the viscosity of the liquid, thereby reducing nucleation and growth rates. For an increase in viscosity by a factor of 2, the nucleation and growth rates each are reduced by half, but the fraction crystallized is reduced by a factor of 16. Since shear in liquid occurs as a result of fluid flow and fluid flow is greatly reduced in low gravity, we have crystallization equations which are affected by gravitational effects.

A number of glass forming liquids have been shown to exhibit shear thinning with an order of magnitude lowering of the viscosity. This is attributed to structural rearrangements in the liquid, and in particular to the orientation of chain like flow units[11]. In phosphate melts, evidence of anisotropic behavior in sheared glass melts is indicated at viscosities less than 10^6 poise, being attributed to the "orientation of the phosphate tetrahedra chains"[12]. Shear thinning in lower viscosity liquids is indicated by molecular dynamics studies of a simple Lenard-Jones liquid consisting of spherical hard spheres. A tendency of the molecules to order themselves into layers parallel to the flow was shown.[13]

At low shear rates, the viscosity of a number of polymer melts increases rapidly at low shear rates due to shear thinning. In order to calibrate our instrumentation, we prepared a known shear thinning liquid composed of the polymer PIB in mineral oil.[14] As one can see from Figure 2, at the lowest measured shear rates the viscosity increases very rapidly with decreasing shear rate.

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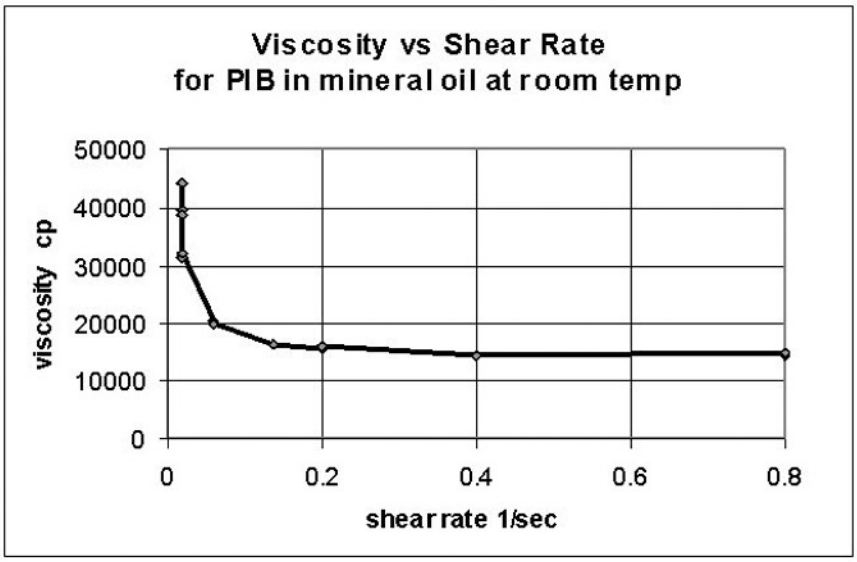

Figure 2. Viscosity vs. shear rate for 6% PIB, polyisobutylene, dissolved in mineral oil.

It is known that flow in undercooled polymer melts initiates crystallization[15]. It is also known that extrusion processing of glass-ceramic glass-forming melts catalyses the nucleation and growth of crystals[16]. Relatively high growth and nucleation rates have been reported in lithium di-silicate melts extruded at 540C where steady state nucleation and growth are practically zero for non-stressed samples[8]. Even though under most conditions glasses exhibit Newtonian viscous flow, non-Newtonian viscous flow has been reported at high strain rates in highly viscous melts[17,18].

Experiments

A vacuum glovebox has been setup to perform crystallization studies of ZBLAN under very high purity atmospheric control, see Figure 3. The vacuum chamber can be evacuated and backfilled with high purity gas, and then an access door opened to provide access with a glove to the experiment. Experiments are being performed with samples under shear stress, in order to determine the effect of shear on nucleation and crystallization.

A rapid thermal analyzer system developed by the PI[19] has been redesigned to examine the crystallization of ZBLAN. The system involves a suspended sample on a Pt thermocouple which is rapidly heated by a halogen lamp controlled by a computer controlled power supply, see Figure 4. Sample temperatures are measured and the system is controlled by Labview software. Because of the low thermal mass of the system, it is suitable for collection of thermal data at rapid heating and cooling rates. It has been utilized for studies of the heterogeneous nucleation of reluctant glass formers[20]. Data will be collected for a range of heating and cooling rates. The time and temperature dependence of transformation and the critical cooling rate under different shear conditions can be determined from the quenching data.

The viscosity of ZBLAN is fairly well characterized over the undercooled temperature range with data from around the melting temperature, around the glass transition temperature, and some measurements in the intermediate range. It has been assumed that the liquid is Newtonian over the entire range. We are developing the methods to measure the viscosity at different shear rates to determine if shear thinning

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occurs in ZBLAN melts at low shear rates. A Rheometrics, Inc. DMTA V has been purchased to perform viscoelastic measurements on ZBLAN, see Figure 5.

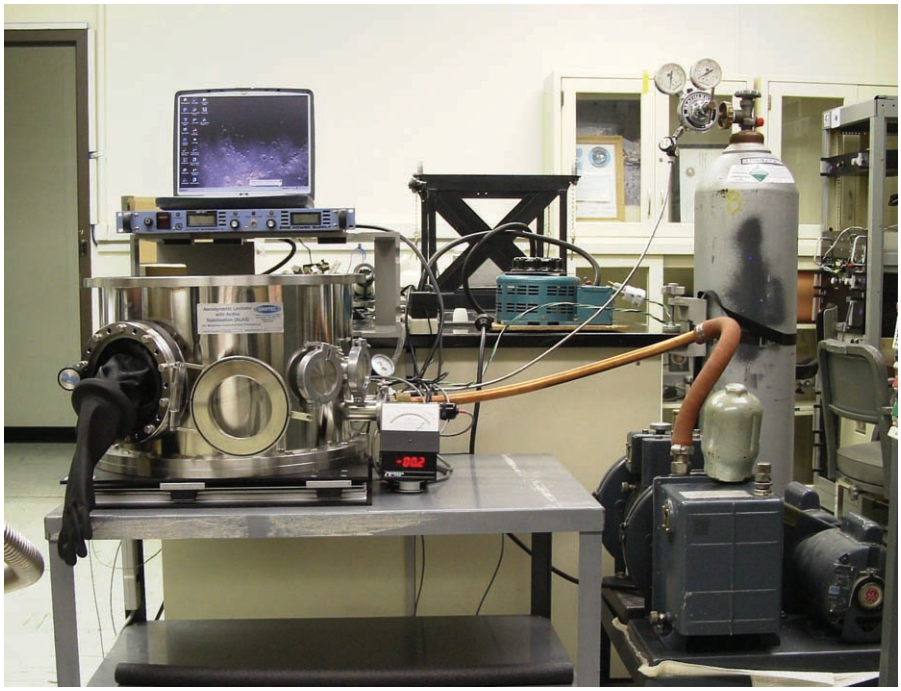

Figure 3. High purity atmosphere control vacuum glovebox.

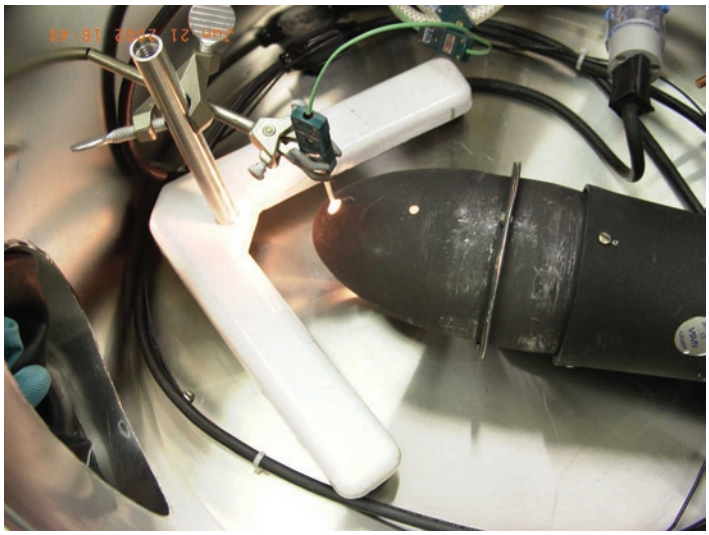

Figure 4. Ellipsoid lamp furnace.

This high temperature Dynamic Mechanical Thermal Analyzer, DMTA, can perform controlled shear, controlled stress, and dynamic viscoelastic measurements on liquids and glasses. Because of certain heat loss problems, it is being redesigned to perform the controlled shear and controlled stress experiments on viscous fluids for viscosity measurements at high temperatures without excessive heat loss, see Figure 6.

Parallel Plate Rheometry is being used to determine the viscosity of glass at very low shear rates. Figure 7 illustrates the test fixture. A constant force squeezes the glass sample. Viscosity is determined from the rate of motion of the parallel plate[21,22].

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Figure 5. Rheometric, Inc. DMTA V

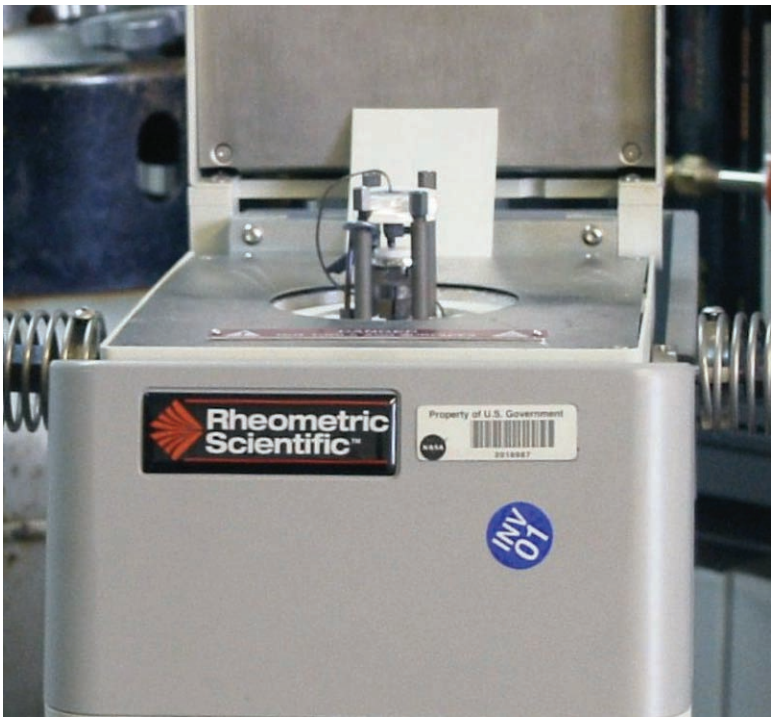

Figure 6. Inside of the DMTA showing the test fixture raised from the furnace.

Lithium di-silicate has been used as a test model material for initial viscosity measurements. Samples were provided by Dr. Delbert Day from the University of Missouri, Rolla. A constant load was applied to the glass and the sample was heated to a controlled temperature. The rate of deflection of the squeezing plates was measured. Data from 4 temperatures is shown in Figure 8.

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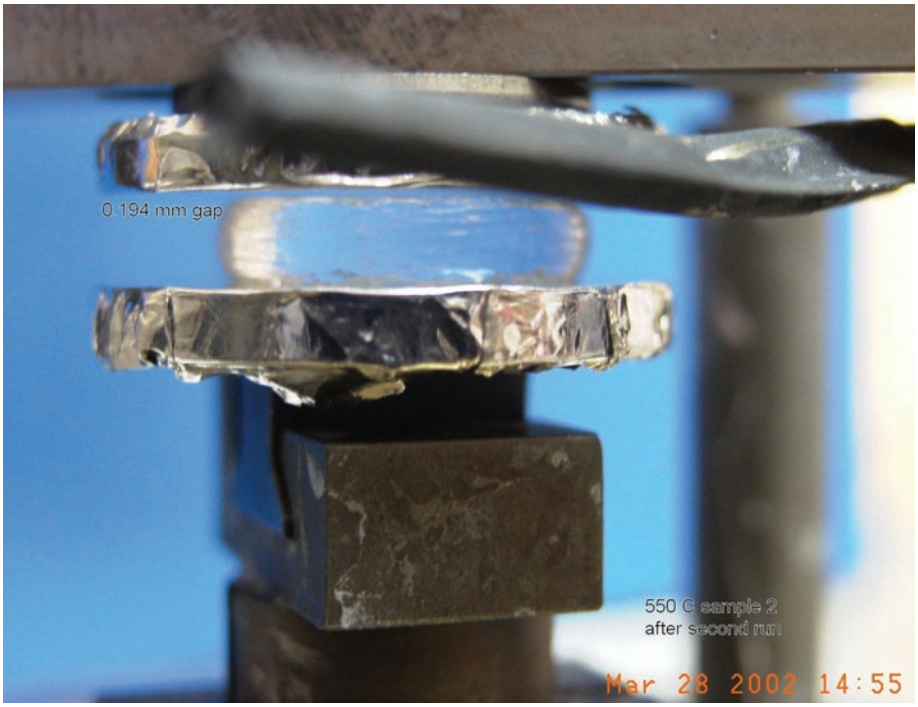

Figure 7. DMTA test fixture for parallel plate viscosity measurements.

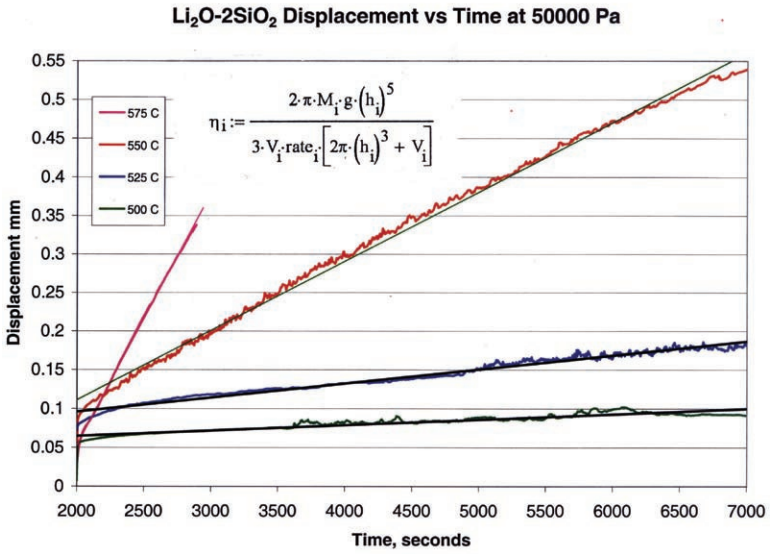

Figure 8. Deflection plots for 4 temperature experiments for Lithium di-silicate glass.

Calculated values for the viscosity are plotted on the graph of Dr. Day's collection of viscosity data from the literature, see Figure 9. The data is above the curve fit to published experimental data. This is consistent with reduced shear thinning in these current measurements, since the shear rate with this parallel plate measurement method is much lower than other measurement methods. The actual glass temperature for these 4 data points is not know as precisely as we would like at this time. We now know that there is significant heat loss through the displacement sensor that lowers the sample temperature by an unknown amount. The sample fixture arrangement is being redesigned to reduce heat loss providing more isothermal experimental conditions. A sample temperature sensor is also being added to the instrument to measure the temperature directly.

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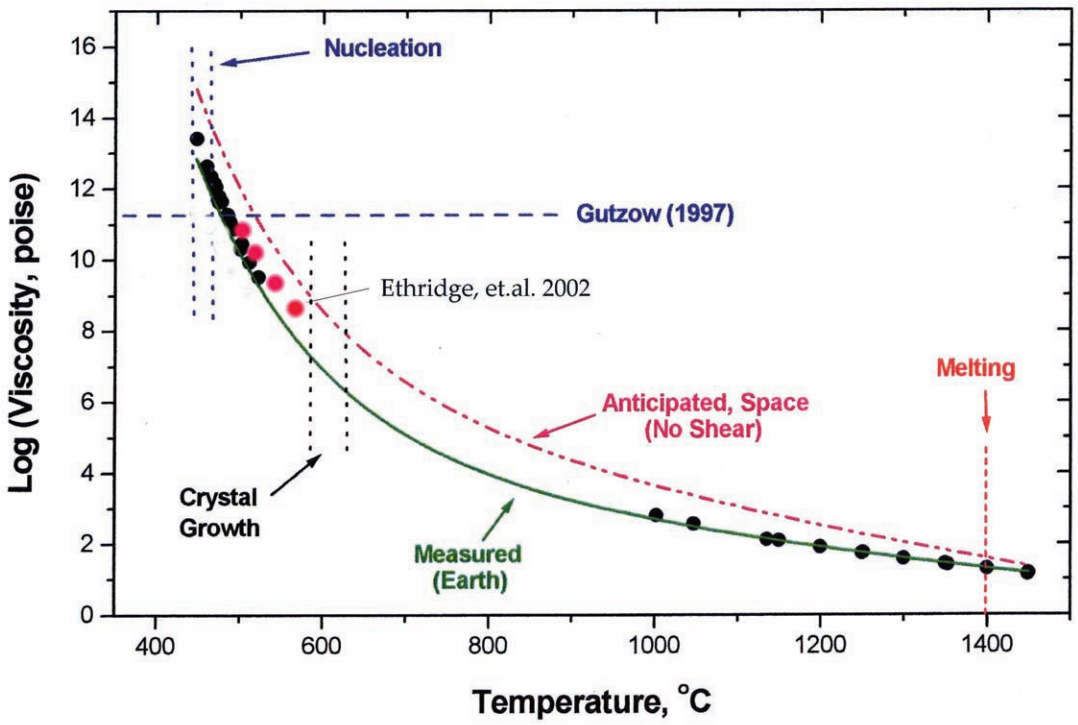

Figure 9. Lithium di-Silicate viscosity data for 4 temperatures, determined from parallel plate viscometry methods plotted on a figure from Dr Delbert Day's Science Concept Review, containing a compilation of data from the literature.

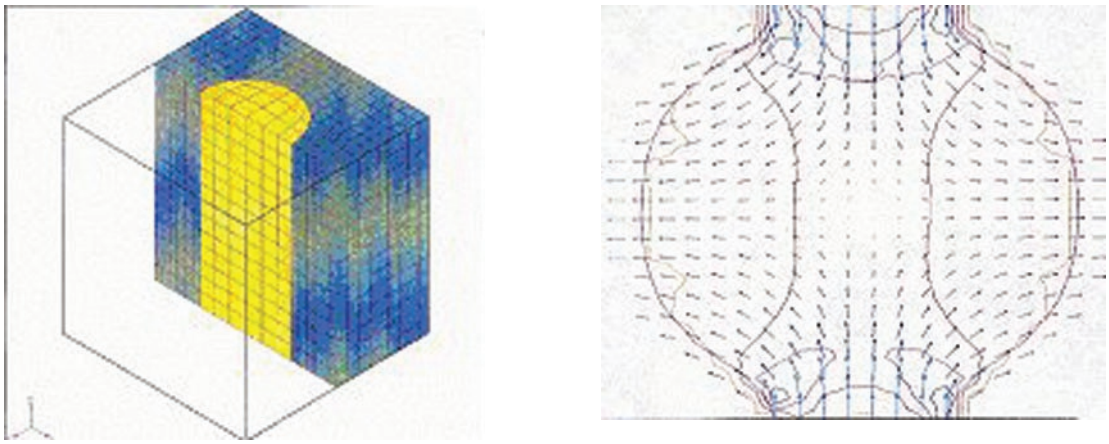

Figure 10. FIDAP fluid dynamic calculations of parallel plate viscometry.

Knowledge of the shear rate in the sample during the viscosity measurement is very important for this study. The experiment is being modeled by Dr. Basil Antar utilizing FIDAP software. The parallel plate squeeze flow experiment used for the above measurements has been modeled by inputing the experimental conditions on the sample, utilizing known materials properties, and the measured viscosity. Flow velocities and shear rates in the viscous liquid are being calculated, see Figure 10. This work will continue with more viscosity measurements and characterization of the shear rates within the samples.

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