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# G-Plus Report to Owens Corning

# Thermophysical Properties of Glasses

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# 1. Introduction

Thermophysical properties of glass are very important for the glass melting and forming processes. These properties are needed for modeling of the glass tank temperature distribution. More importantly, a good understanding of the thermophysical properties will also affect the productivity, energy and raw material cost.

It has been well documented that thermophysical properties data of the glasses are difficult to measure, especially into the melt region. In this project, we tested glass samples provided by Owens Corning for thermal diffusivity, thermal conductivity, specific heat and thermal expansion from room temperature to Tg and above. The thermal conductivity measurements into the glass melt (above 1000ºC) were not achieved using the current laser flash technique and other available instruments. A specially designed probe is needed for measurement in melt of 1200-1600ºC. As far as we know, there has been no commercial testing device that can accurately measure thermal conductivity of glass melts. Thermal expansion and heat capacity results both showed the glass transition temperature consistently. All the measurements indicated Tg near 780ºC.

# 2. Experimental

## 2.1 Glass Specimens:

The specimens were provided by Owens Corning in the form of 2" diameter blocks. Six samples of the same composition were received. This type of glass has been used in production of fiberglass at Owens Corning. The specimens were cut and machined at ORNL to meeting various measurement needs. The original samples were used for Hot Disk thermal conductivity measurements. Disks of 12.5 mm in diameter and 1 mm thick were used for thermal diffusivity measurements, while disks 6 mm in diameter and 1 mm thick were used for heat capacity tests. For the thermal expansion test, rectangular bars 3 mm x 4 mm x 25 mm were used.

Figure 1. Glass samples provided by Owens Corning

## 2.2 Thermal Diffusivity:

Thermal diffusivity of the glass was tested using an Anter Laser Flash Thermal Diffusivity (LFTD) system as shown in Figure 2. The rod samples, 12.5 mm, in diameter were core drilled from the original block. Then, 1 mm disks were sliced from the rod. Since the glass is transparent to both the laser light and infrared detector, graphite coatings were spayed on both surfaces to prevent light penetration. The laser flash system has the ability to measure thermal diffusivity up to 2400ºC. The same system was used to measure diffusivity of molten steels using a specially designed cell. However, due to the transparency of the glass, the same cell could not be used. Coating the sample is not a practical solution. We measured thermal diffusivity above the Tg point until the deformation due to softening affected the measurements.

Figure 2. Laser flash diffusivity unit at ORNL.

## 2.3 Thermal Conductivity:

Thermal conductivities of the glass samples were obtained by two methods: 1) calculate from thermal diffusivity and specific heat data and 2) use the Hot Disk method. The thermal conductivity, k (W/mK), calculation uses the following equation:

$$k = 100\alpha C_p \rho \qquad (1)$$

where $\alpha$ is thermal diffusivity ($cm^2/sec$), $C_p$ is the specific heat (J/gK) and $\rho$ is the density ($g/cm^3$).

For the direct measurement of thermal conductivity, the Transient Plane Source method was used [1-3]. The Hot Disk system based on this method is shown in Figure 3. The upgraded system uses a bridge circuit to measure the temperature change of the sensor during heating. The heating and sensing were accomplished using a double-spiral nickel

heater sandwiched between two thin mica sheets. The mica sensor allows measurements up to 800ºC. Figure 4(a) and (b) are high temperature sample holder and box furnace used for the measurements.

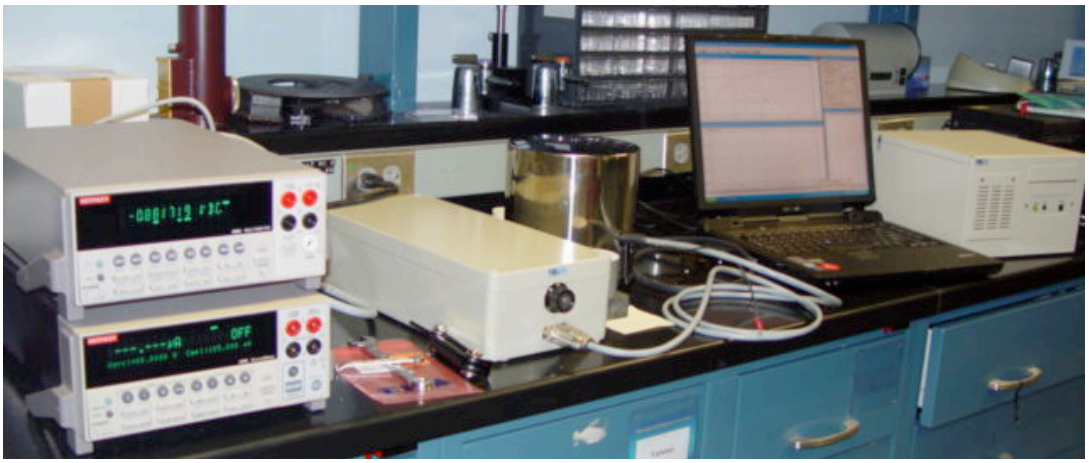

Figure 3. Upgraded Hot Disk thermal constants analyzer at ORNL.

(a) (b)

Figure 4(a) High temperature Hot Disk sample holder; 4(b) Box furnace for high temperature thermal conductivity measurements.

**2.4 Specific Heat:**

Specific heat measurements were conducted using the differential scanning calorimeter (DCS) system manufactured by Netzsch Instruments Inc.. The technique, ASTM E1269, is based on measurement of the thermal response of an unknown specimen as compared with a standard when the two are heated uniformly at a constant rate.

To determine specific heat capacity, a baseline is established by measuring the temperature difference of the two empty crucibles as the temperature is changed at a constant rate over the temperature range of interest. Thermal response records are then acquired for a standard material (usually sapphire) and an unknown under identical

conditions. The ratio of the departure of the standard and unknown from the baseline is then used to calculate the specific heat of the unknown.

**2.5 Thermal Expansion:**

Thermal expansion of the glass was measured using a differential push rod dilatometer, which measures linear thermal expansion from 20°C up to 1600°C. The thermal expansion of a test specimen is determined relative to that of a standard reference specimen. The two specimens are placed side by side in a furnace and two alumina push rods that extend from the furnace to a thermally isolated linearly variable displacement transducer (LVDT) bear on the specimens.

A difference in expansion between the two specimens results in a differential movement of the push rods, thus allowing the linear thermal expansion of the unknown sample to be determined. The temperature of the specimen is measured with a Pt vs. Pt-10Rh thermocouple to a resolution of 0.1° C.

## 3. Results and Discussion:

**3.1 Thermal Diffusivity Results:**

Thermal diffusivity of the glass was measured from room temperature to 1000ºC using the laser flash system. The tests were conducted in two furnaces: from room temperature to 500ºC in an aluminum furnace and from 700-1000ºC in a graphite furnace. Since glass is transparent/semi-transparent for both the laser (Nd:YAG) and the detector (InSb), we coated the surface with a submicron graphite coating to prevent penetration. Figure 5 shows the low temperature thermal diffusivity data of two glass specimens. The results showed very good agreement among duplicates.

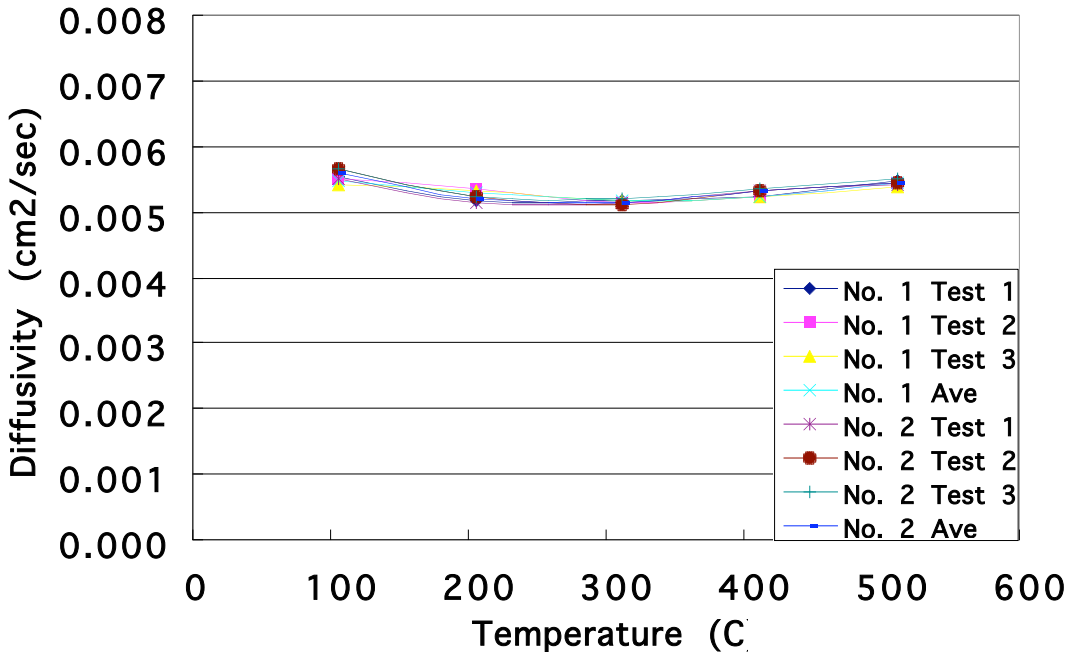

Figure 5. Thermal diffusivity from 100ºC to 500ºC of two glass samples.

However, when the high temperature diffusivity tests were conducted, it was noted significant laser penetration and surface-to-surface radiation occurred. As shown in Figure 6, the thermal transients at 686ºC, 748ºC, 797ºC and 999ºC showed increasing amount of initial direct radiation. This effect occurs in glasses and ceramics. The effect on the final thermal diffusivity value can be neglected whenever the initial "jump" is less than 10% of the total signal. Figure 6 shows the effect cannot be ignored after 700ºC.

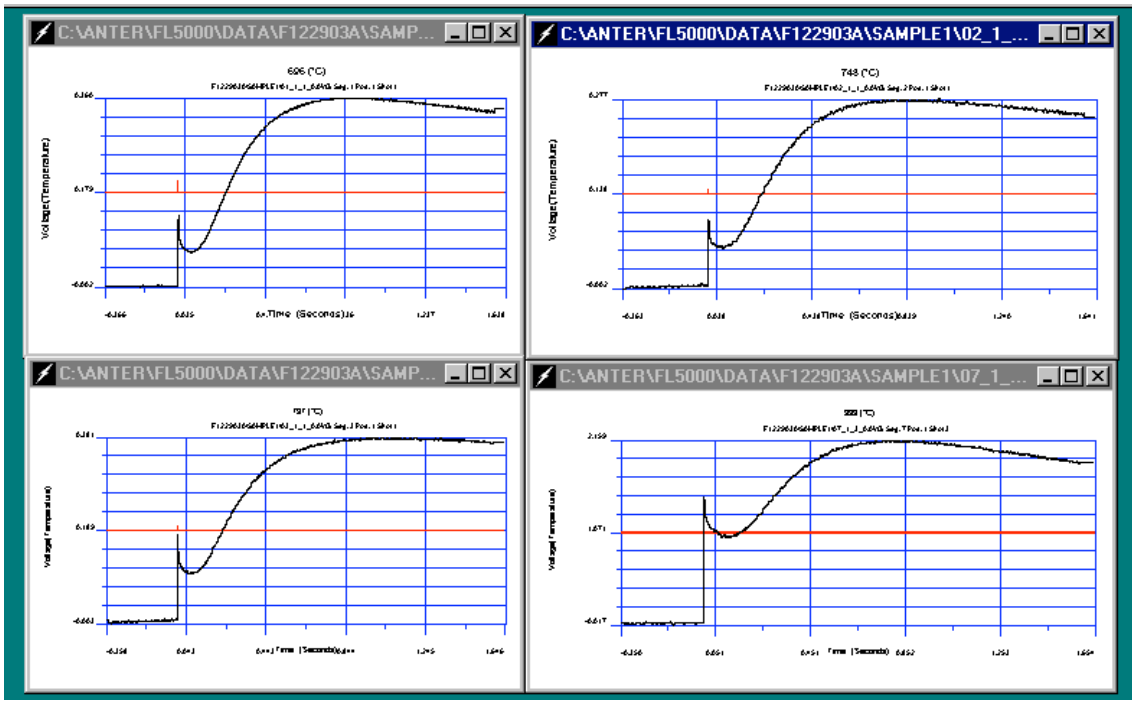


Figure 6. Diffusivity transients showing the effect of radiation and light penetration.

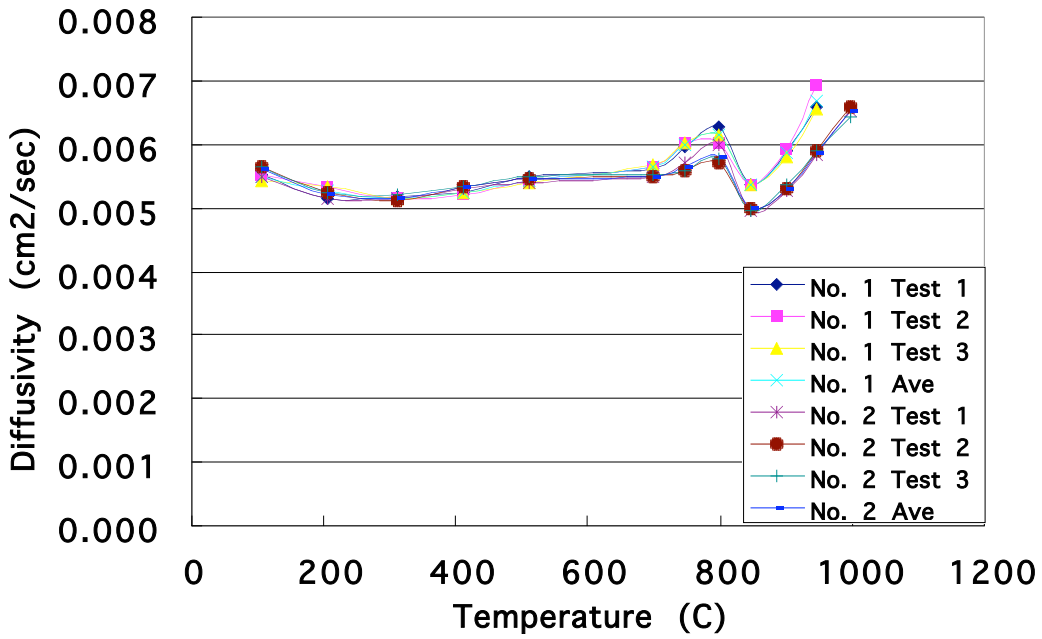


Figure 7. Thermal diffusivity of glass up to 1000ºC

Considering this effect, we chose the Koski-Cowan [4] analysis in calculating the thermal diffusivity. This method uses the trailing edge of the transient to calculate thermal diffusivity. Since the heat transfer portion of the transient happened later in time, the Koski method gave reasonable continuity at 500-800ºC. As shown in Figure 8, thermal diffusivity showed a decrease after 800ºC and recovered the loss in value in 900-950ºC. This change indicated the glass transition temperature range. Thermal diffusivity measurements were able to continue to 1000ºC. The sample became concaved due to softening. But the rapid change in diffusivity after $T_g$ may be due to the fact that not all the heat input was used in one-dimensional heat transfer, and therefore the laser flash method became inadequate of measuring the diffusivity of the glass melt.

**3.2. Thermal Conductivity(Hot Disk) Results:**

Thermal conductivity of the glass was also measured directly using the Hot Disk system. Two bulk glass samples similar to the one shown in Figure 1 were used. At room temperature, i.e. 20ºC, thermal conductivity, thermal diffusivity and volumetric heat capacity of the glass were measured. The heating power was 0.4W and heating duration was 20 seconds. As shown in Table 1, thermal properties of the glass can be obtained in one test. The results were very reproducible under the same test conditions.

To make the same measurements at higher temperatures, the high temperature holder and a box furnace were used. Since the thermal diffusivity and heat capacity were obtained from curve fitting, the values are not as reliable as thermal conductivity. If the heat capacity is known, thermal diffusivity values could be accurate. We only show the thermal conductivity results in Figure 8. The measurements became difficult after 300ºC. The scatter due to noise increased with temperature.

At 400ºC and above, the contact between the sensor and leads often became loose due to thermal expansion of the parts. The sensor usually cannot be reused after high temperature exposure. We conclude that the Hot Disk system is best for measurements of room temperature and modest high temperatures. The idea of using similar sensor can be further explored for glass melt application. The current mica/nickel/mica sensor is not suitable for this type of measurement.

Table 1. Room temperature thermal properties of the Owens Corning glass specimen.

| Test Number | K (W/mK) | A ($cm^2$/sec) | Cp ($MJ/M^3K$) |
|---|---|---|---|
| 1 | 1.228 | 0.006080 | 2.019 |
| 2 | 1.227 | 0.006113 | 2.013 |
| 3 | 1.230 | 0.006044 | 2.031 |
| 4 | 1.228 | 0.006114 | 2.020 |
| 5 | 1.230 | 0.006081 | 2.013 |
| Average | 1.229 | 0.006086 | 2.019 |

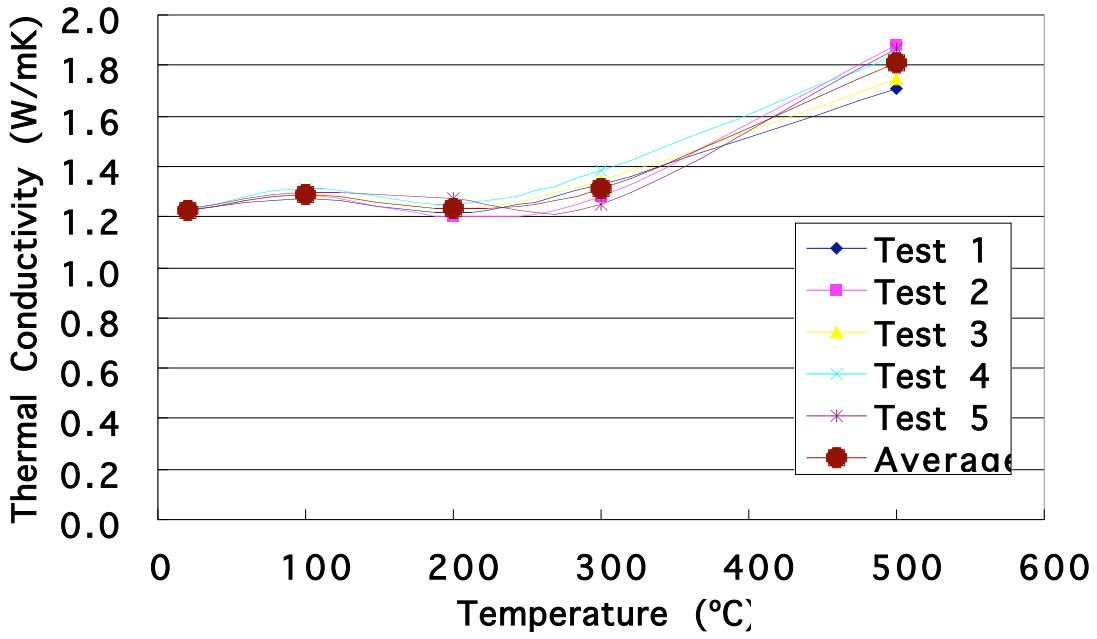


Figure 8. Thermal conductivity of the glass using the Hot Disk method.

**3.3 Heat Capacity Results**

Specific heat capacity of the glass was measured at the heating rate of 20ºC/minute and cooling rate of 20ºC/minute. The test included an empty pan run and a reference sample (sapphire) run. The maximum heating temperature was 900ºC.

As illustrated in Figure 9, the heat capacity showed a peak upon heating at about 765ºC with onset just above 720ºC. During cooling the change in slope occurred at about 780ºC and ended around 650ºC. These temperature dependent features were reproducible and are typical for glasses. The glass transition temperature, Tg, is consistent with the thermal diffusivity changes in the same temperature range. Since the thermal diffusivity tests were conducted with 50ºC interval, the DSC results are considered a better indication for glass transition. We did not go into detailed analysis of Tg since this was not the objective of the project.

The heat capacity data were used to calculate thermal conductivity indirectly using Equation (1). We used the heating Cp data and curve fitting to obtain values at the exact temperature of thermal diffusivity measurements. The density of the glass is assumed to be unchanged in the temperature range. This is a valid assumption since the experimental uncertainty (5%) is larger than the error caused by thermal expansion of the specimen. Figure 10 shows the calculated thermal conductivity and Hot Disk results. It is clear the agreement at low temperatures (below 300ºC) is acceptable, although it showed consistent higher thermal conductivity values (3-5% higher). This could be because of systematic error introduced by the mica sensor. However, the Hot Disk result at 500ºC is

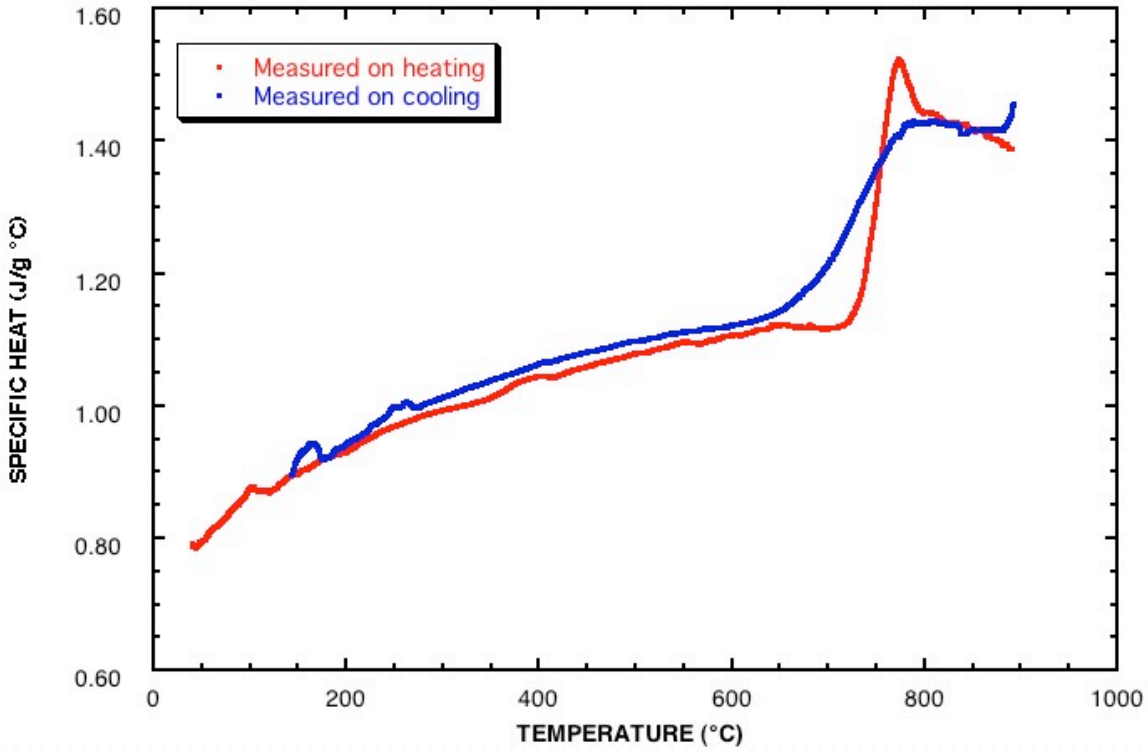

Figure 9. Specific heat of the glass

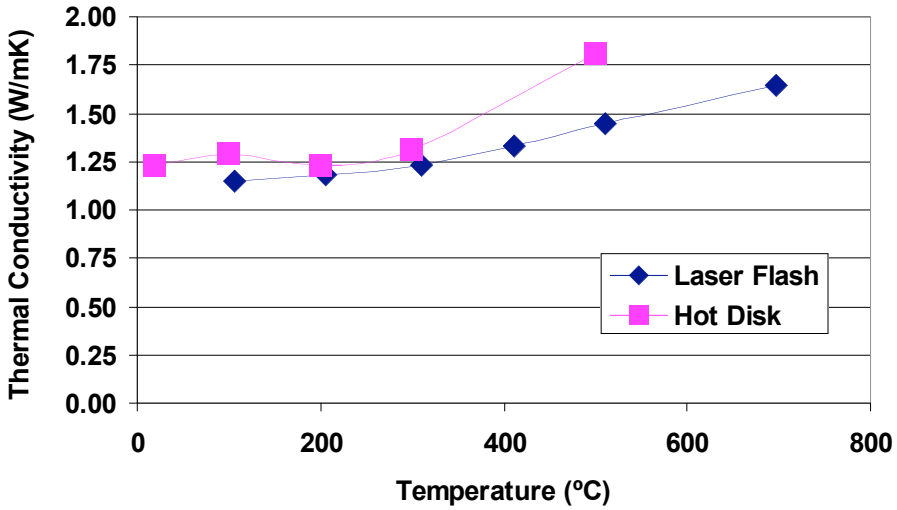


Figure 10. Thermal conductivity of the glass measured by two methods.

highly questionable. A phase transformation of the nickel heater between 300-400ºC may have caused further decrease in sensitivity. It was unrealistic to adjust the sample holder and electrical connection once the sample is at high temperature. The mica sensor, glued by adhesives, may not show repeatable response upon high temperature exposure. The accurate temperature range for the Hot Disk method should be below 300ºC.

**3.4 Thermal Expansion Results:**

Thermal expansion of the glass was measured using a push-rod dilatometer. The linear thermal expansion result is shown in Figure 11. The thermal expansion is linear from room temperature to about 600ºC, at which the slope began to change. Using the slope change after 700ºC we estimate the glass transition occurred about 720ºC. This was consistent with DSC results as well and the thermal diffusivity measurements. The load on the sample was 30 g. The experiment stopped when the sample buckled under the load. The behavior shown in Figure 11 is typical for glasses. Mean coefficient of thermal expansion is calculated using $(\Delta L/L_0)/\Delta T$. The coefficient vs. temperature is shown in Figure 12.

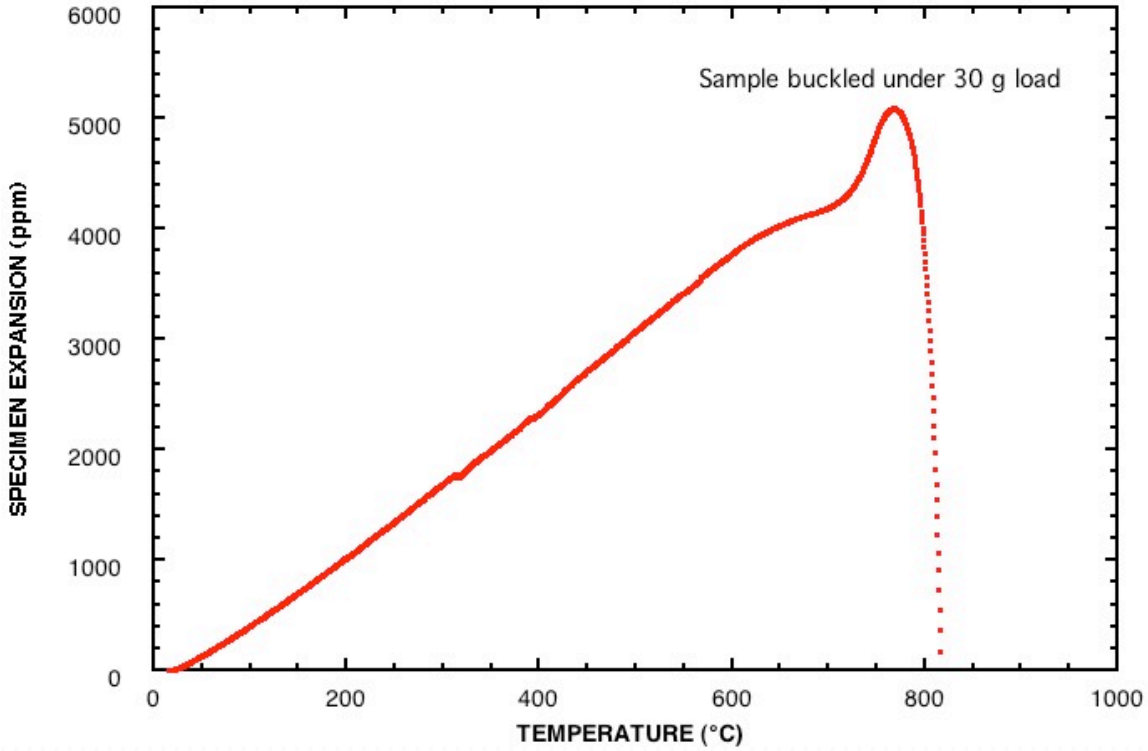

Figure 11. Linear thermal expansion of Owens Corning glass

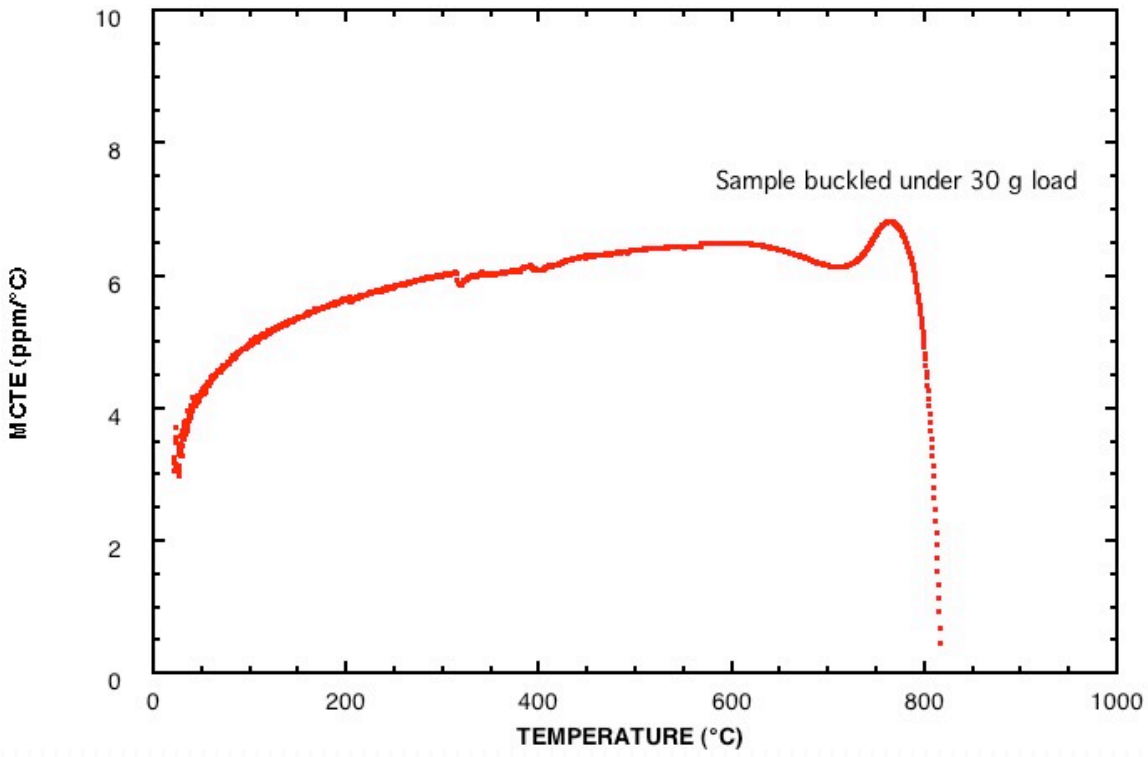

Figure 12. Mean coefficient of thermal expansion of Owens Corning glass

## 4. Suggested Thermal Property Measurements of Glass Melt

**Thermal Conductivity:** Traditional thermal conductivity measurements cannot be used to measure glass melt. Although the laser flash method has been used for molten metals, it could not overcome the problem of transparency. In addition to this, glass transition covers a large temperature range. It is difficult to apply a heat pulse (via laser) and insure all the energy will be transmitted to the other side via heat conduction. To our knowledge, there is no commercially available device to measure thermal conductivity of glass melt. The most promising device is a disposable probe used by Professor R. Conradt of Germany [5]. Significant development is needed to develop a reliable probe for long monitoring of thermal conductivity of glass melt.

**Thermal Radiative Properties:** Since glass melt maintains temperature well above 1000ºC, its radiative properties can be monitored and related to the properties of the final products. Emittance or spectral emissivity of the glass melt can be used to reflect change in temperature or composition. The current equipment in our laboratory does not cover the required wavelength range necessary for glass melt monitoring. However, we feel the best way to obtain glass melt properties is via non-contact means.

## 5. Summary:

Thermal properties of Owens Corning glass were studied. The laser flash method, DSC and thermal expansion results all indicated the same glass transition region. Thermal properties into the melt were only achieved to 1000ºC. At higher temperatures, all the current experimental setup could not be used. Special thermal conductivity probe has to be designed to measure thermal conductivity of the glass melt. Heat capacity of the glass melt could be measured when proper sample container is chosen.

## Acknowledgement:

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