A Thesis Presented to

The Faculty of Alfred University

Colorless Glass with Ultraviolet Fluorescence

by

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Non-technical Prologue

Glass is an amorphous, usually inorganic, solid. Commonly it contains components, other than carbon, in a disordered pattern. For example non-amorphous, or crystalline, materials repeat in a predictable pattern of planes of atoms. Glass, however, bonds less orderly in different size rings and looks like a liquid frozen into place. It is this amorphous lack of structure helps glass to be transparent.

As light travels through the glass it interacts with the electrons in atoms. Light can be absorbed, reflected, or scattered by electrons. In other words light is captured or direction changed by the atoms' electrons. Sometimes light energy outside the visible range is absorbed then reemitted at a different wavelength inside the visible range. Wavelength is the distance between peaks of a wave; and is important because it relates to the amount of energy transferred by the wave. The change in wavelength caused by interactions with atoms is an essential part of fluorescence.

There are several ways light can interact with the atoms in glass, and each has a technical term. Luminescence refers to all non-thermal production of light. Photoluminescence is when radiation produces light emission in the visible range. Fluorescence is rapid photoluminescence; in other words instantaneous

production of visible light when a substance is exposed to electromagnetic radiation. Rare earth ions exposed to ultraviolet light can emit the energy back in longer wavelengths as visible light. Since this happens instantaneously upon addition and removal of the ultraviolet source, it is concluded that rare earth ions fluoresce.

These interactions are marketed to the public with phrases like, “glow-in-the-dark” or “black light activated”. Glow-in-the-dark products which need to be held to a light, “charged”, before they glow is actually slow photoluminescence. Eventually the atoms will run out of stored energy and the product will stop glowing. Black lights are mainly ultraviolet light, which has a higher energy and shorter wavelength then visible light. Products that are black light activated fluoresce due to the fact that their glowing color only occurs when directly under the energy source. Fluorescent glass would act like the black light products when exposed to the ultraviolet light, but seem like regular clear glass in visible light.

Glass is made from different elements, and the key “ingredient” for fluorescent in these samples of glass are rare earth ions. Rare earth elements occur together in the third group of the periodic table. All of the rare earth elements are more abundant than gold, but are called rare due to the difficult mining process

they must go through to be extracted from the earth. They are commonly referred to as rare earth oxides, due to the fact that they are usually sold as oxides instead of pure metals. This is because rare earth elements are mined as compounds, and the process to separate them into pure metals is very expensive. The seventeen elements which are considered rare earth elements all have f-subshell electron configuration. Due to this atypical electron configuration, rare earth elements are used in electronics, alloys, magnets, and more. The variety of f-subshell electron transitions with energies in the visible range is what facilitates fluorescence in rare earth ion containing solids.

One main use for ultraviolet fluorescent glass would be art. This glass could offer glass artists a new dimension to work with. Optical properties of glass are a major factor when a glass artist designs a piece. In normal (visible) lighting a piece can look very different than in ultraviolet light. This duality can be utilized to convey deeper concepts than one type of lighting could. Juxtaposition and interaction between the two lightings both allow the artist more channels for expression. There is also something mystical about the color given off in ultraviolet light. The color is created by the glass, so instead of reflecting light it is creating light. Your eye senses this as you recognize that the piece is glowing. Our brains have been trained by culture to link glowing to magical and supernatural powers. Artwork can give the viewer a sense of supernatural presence by the

fact that it is glowing. There are most likely numerous other uses an artist could come up with for using fluorescent glass.

For this experiment, I batched glass compositions and tested them to reveal the optimal composition of ultraviolet fluorescent glass. Batching glass is similar to baking cookies. I used System 96 as the base glass composition; this can be seen as a box cookie mix. I then varied the rare earth oxides, i.e. chocolate chips, to find what amount was ideal. The first group of samples had different rare earth oxides, but constant concentration. From this samarium oxide was chosen for further compositional analysis due to its bright fluorescence and intriguing peachy color. The second group of samples only had samarium oxide added to the System 96, but the concentration was varied. These samples were tested on brightness of fluorescence, thermal expansion, and cost. The result is that composition 9, which is 0.8g of samarium oxide to 100g of System 96 frit, is the optimal composition created. Composition 9 is compatible with System 96 in terms of thermal expansion. This composition is also has the highest fluorescence intensity of the compositions tested. The price may seem high, but the fluorescence effect goes a long way in making a statement. In the end composition 9 should be scaled up and used by artists.

I. Executive Summary

Rare earth ions experience fluorescence since they have a variety of f-subshell electron transitions with energies in the visible range. This fluorescence property can be observed in glass if the rare earth ion is added to the melt constituents. Standard System 96 glass frit acted as the glass composition basis to which various rare earth ions were added. The goal was to find a rare earth ion, and corresponding concentration, which would have significant intensity of visible fluorescence when excited by ultraviolet light, while remaining clear under visible white light. The first group of added oxides included the rare earths: praseodymium, dysprosium, cerium, lanthanum, and samarium. The spectra of the resultant glasses were analyzed under ultraviolet and visible light. Samarium had the most pronounced color under ultraviolet light while remaining clear in visible light. Samarium was thus chosen for subsequent evaluation. The concentration of samarium in System 96 glass was varied and the thermal expansion, photoluminescence, and cost evaluated. It was concluded that the optimal glass composition for art purposes is 0.8wt% of samarium oxide (Sm_2O_3) in System 96 glass frit. This composition has a compatible thermal expansion with System 96, is reasonable in cost, and has the brightest fluorescence.

II. Introduction

Glass is an ancient material which still intrigues people to this day. Glass is most commonly used for its optical properties. Artists who mainly work with glass know that lighting a piece can greatly affect the viewing experience of the observer. It would be interesting for a piece to look like basic clear glass in normal lighting, but once lighting switches to black light (ultraviolet light), the piece would glow a color in the visible range. This glass is possible if the composition contains rare earth ions. In this report rare earth oxides including: praseodymium, dysprosium, cerium, lanthanum, and samarium were explored due to availability and cost. Samarium oxide was then chosen for further optimization, in terms of thermal expansion compatibility, cost, and fluorescence intensity, due to the intriguing color it fluoresces.

III. Background

Rare earth elements occur together in the third group of the periodic table. All of the rare earth elements are more abundant than gold, but are called "rare" due to the difficult mining process they must go through to be extracted from the earth.[1] They are commonly referred to as rare earth oxides, due to the fact that they are usually sold as oxides instead of pure metals. This is because it is an expensive process to remove the rare earth metals from the compounds they are in when mined. The seventeen elements which are considered rare earth elements all have f-subshell electron configuration. Due to this atypical electron configuration, rare earth elements are used in electronics, alloys, magnets, and more. The variety of f-subshell electron transitions with energies in the visible range is what facilitates fluorescence in rare earth ion containing solids. However it is highly unlikely that energy will excite to these specific energy states directly, so the rare earth ions appear clear in visible light.

Energy absorbed by an atom must be released eventually in the form of an electromagnetic wave. Luminescence refers to non-thermal production of light. Photoluminescence is when high energy radiation produces light emission in the visible range. Fluorescence is rapid photoluminescence; in other words instantaneous production of visible light when a substance is exposed to radiation.[2] Many rare earth ions exposed to ultraviolet light emit the energy back in longer wavelengths as visible light. Since this happens instantaneously upon addition and removal of the ultraviolet source, it is concluded that rare earth ions fluoresce. By adding rare earth oxides to glass melt constituents, it is hypothesized that the glass would also have this fluorescence property. This composition could then be optimized to be compatible with common art glass (System 96), have high fluorescence intensity, and reasonable cost.

IV. Sample Preparation

A 5lb bag of System 96 glass studio nuggets was received from the Alfred glass art department, and used as the base glass composition. Nuggets were crushed using a mortar and pestle until the largest particle was about 5mm in diameter. A 100g of crushed glass was measured out, and to this rare earth oxides were added. Since System 96 is a commercial glass and the exact composition is a trade secret, weights were used for measuring instead of mols. The first batch of samples included different rare earth oxides as seen in Table 1. For these samples the amount of rare earth oxide was held at a constant 1g to the base of 100g glass frit. The powdered mixture was then melted to the specifications in Table 2.

Table 1: Different rare earth oxides in System 96 glass frit

	Rare Earth Oxide	**Oxide (g)**	**System 96 frit (g)**
Sample A	Praseodymium	1	100
Sample B	Samarium	1	100
Sample C	Dysprosium	1	100
Sample D	Cerium	1	100
Sample E	Lanthanum	1	100

Table 2: Sample melting specifications

Crucible type	Mullite
Furnace	Lindberg box furnace
Furnace Temperature	1250°C
Time in Furnace	1 hr.
Annealer Temperature	540°C
Time in Annealer	2 hrs.

Visual inspection of samples A - E, indicated samarium oxide as the best rare earth oxide to do a more in depth compositional analysis of due to it remaining clear in visible light and

producing a stunning and intense fluorescence color. Figure 1 shows the first batch of samples in both visible and ultraviolet light. The samarium oxide has vivid fluorescence and interesting color, so it was chosen for further study.

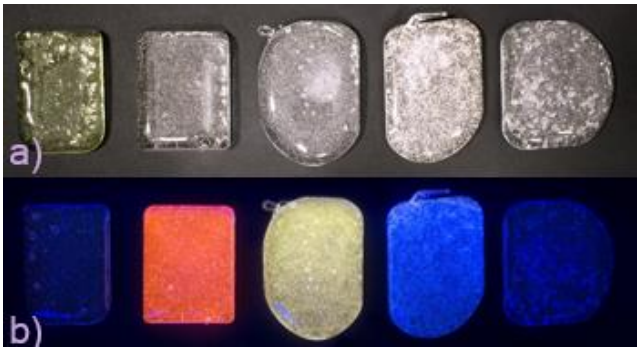


Figure 1: Rare earth oxides (1g) in System 96 frit (100g) in a) visible light, b) ultraviolet light. From left to right samples containing the rare earth ion: praseodymium, samarium, dysprosium, cerium, and lanthanum.

A second batch of samples was melted, using the same specification as listed in Table 2. This batch only contained samarium oxide (Sm_2O_3) and System 96 frit. The samarium oxide content was varied, while the 100g of frit was held consistent. This created a range of samarium oxide concentrations which can be seen in Table 3.

Table 3: Samples with range of samarium oxide concentration

	Sm_2O_3 (g)	**System 96 frit (g)**
Composition 0	0.00	100
Composition 4	0.20	100
Composition 5	0.10	100
Composition 6	0.50	100
Composition 8	0.65	100
Composition 9	0.80	100
Composition 10	1.00	100
Composition 11	3.00	100

Again samples were visually inspected in both visible an ultraviolet light, as seen in Figure 2. When lined up in increasing samarium oxide concentration it appears that fluorescence intensity increases with Sm_2O_3 concentration increase. However this is an optical illusion and more technical testing must be performed. These samples were prepared for thermal expansion and photoluminescence testing.

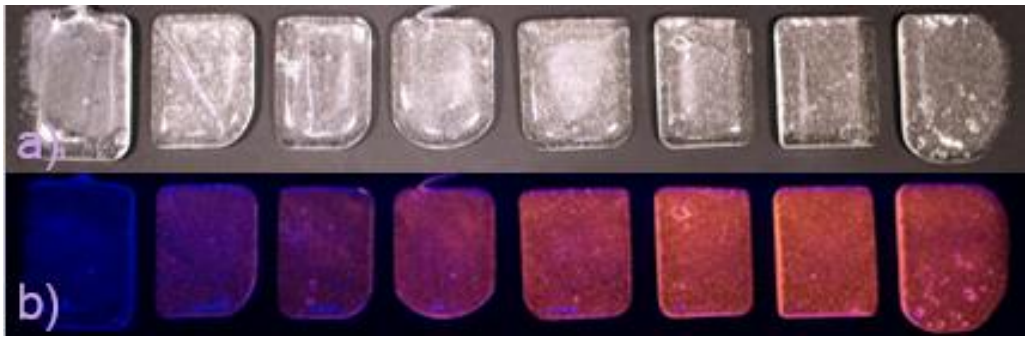


Figure 2: Increasing samarium oxide concentration in System 96 frit a) visible light, b) ultraviolet light. Amount of Sm_2O_3 from left to right: 0g, 0.1g, 0.2g, 0.5g, 0.65g, 0.8g, 1.0g, and 3.0g.

The range of samarium oxide concentration glasses were cut and polished for thermal expansion coefficient and photoluminescence measurement. Samples for the dilatometer were cut and polished so that they were a rectangular prism with parallel sides roughly 1in long. The actual length for each sample is listed in Table 4. For photoluminescence testing samples were created having polished parallel sides, with a surface area more than $1cm^2$. Samples were polished using the schedule listed in Table 5.

Table 4: Length of dilatometer samples

	Length (mm)
Sample 0	22.64
Sample 4	26.89
Sample 5	25.70
Sample 6	20.51
Sample 8	26.91
Sample 9	21.62
Sample 10	25.69
Sample 11	19.76

Table 5: Polishing schedule of photoluminescence samples

Grit	**Time (min)**
120	10-20
240	5
320	5
400	4
600	4
800	2
1200	2

V. Experimental Procedure

Thermal expansion coefficient was measured using a Dilatronic (theta industries, Inc.) dilatometer. The dilatometer measures the expansion of the sample as a function of temperature. Figure 3 shows the inside setup of the dilatometer, before pushrods are moved into position. A standard of silica glass is placed in the front so that the expansion of the silica push rods can be subtracted from the sample reading which is taken in the back. As samples expand they apply a force to the pushrods which a detector measures and records. Each sample was heated to 550°C with temperature ramp of 3.0°C/min and expansion measurements taken every 0.1 min.

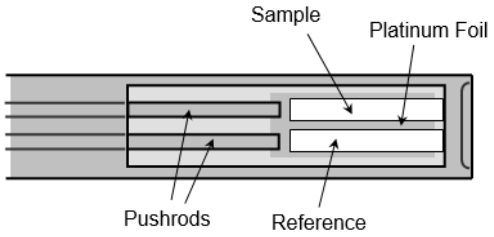


Figure 3: Dilatometer Set-up[3]

From the dilatometer data, equation 1 can be used to calculate the linear thermal expansion coefficient. If the data is plotted, expansion vs. temperature, then the slope of the linear region is the thermal expansion coefficient.[4]

Equation 1: Coefficient of Thermal Expansion

$$\text{CTE} = \frac{1}{Sample\ length(mm)}\left(\frac{\Delta length\ (mm)}{\Delta temperature\ (K)}\right)$$

The photoluminescence of each sample was measured using a Fluorolog® Tau-3 Lifetime System. Figure 4 shows a schematic of the instrument.[5] Light travels from the source through an excitation monochromator which selects the specific wavelength that will hit the sample. The sample is excited by the incident radiation and emits a new longer wavelength. This new wavelength passes through an emission monochromator and into the detector. The measurement is sensitive to surface flaws as it is focused to the assumed flat surface of the sample.

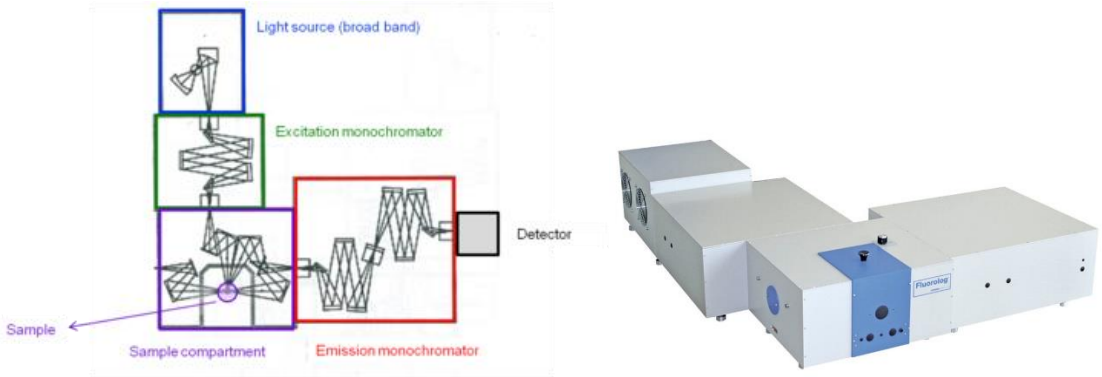


Figure 4: Energy pathway diagram (left) and image (right) of Fluorolog® Tau-3 Lifetime System

VI. Results and Discussion

Figure 5 shows the thermal expansion coefficient for each sample as a function of samarium oxide concentration. Thermal expansion coefficients were calculated form measured dilatometer data, and individual expansion curves can be found in the appendix. System 96 claims to have a thermal expansion of 9.6 ppm/K with ±0.2 compatibility range.[6] However the control sample, containing no samarium oxide, has a measured thermal expansion coefficient of 10.36 ppm/K. This can be attributed to the fact that glass properties are sensitive to thermal history. Due to this, composition 0 was held as the compatibility median with ±0.2 ppm/K being the green compatibility range. Compositions 6-10 fall in the green compatibility range. This means that these compositions can be used along with any other System 96 glass. Remaining compositions are outside the compatibility range, which does not mean it cannot be used with System 96. However, it means that if used with System 96 glass special annealing would be required to prevent cracking, which the other compositions would not need.

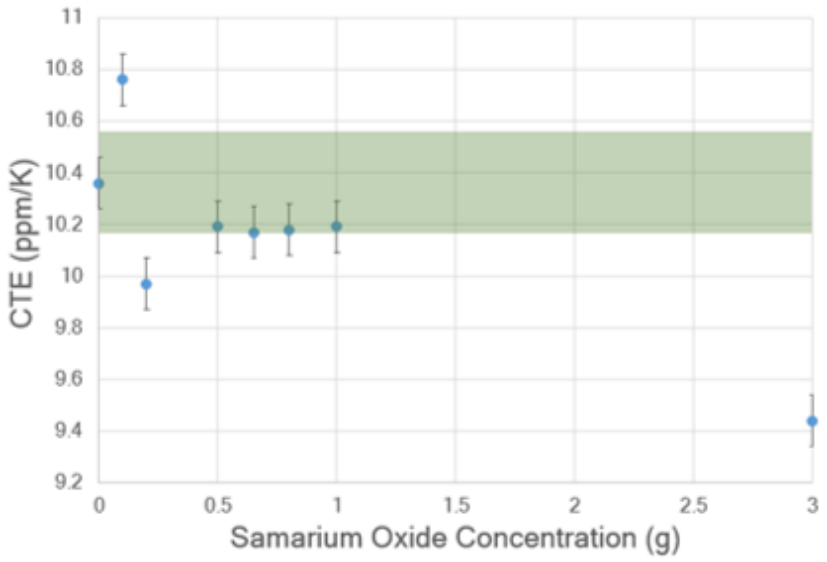


Figure 5: Thermal expansion coefficient as a function of samarium oxide concentration.

(Green region= System 96 compatible)

It is difficult to distinguish fluorescence intensity with the naked eye, especially when looking at compositions 9-11. Each composition fluorescence was measured with the same incident spectrum, and the resulting intensities recorded in Figure 6. The readings have similar peak shape and locations, which is expected as samarium oxide is the cause of fluorescence in all of them. The variation is seen in intensity of emitted wavelength. Composition 9 has significantly higher fluorescence intensity. As samarium oxide concentration increases there should be a maximum emitted intensity. There is some point at which emitted energy is absorbed by the neighboring rare earth ion and is not emitted from the sample, thus not measured by the detector. This is referred to as fluorescence quenching.[7] Figure 7 shows this trend more clearly by focusing on the 600nm emission peak. The fluorescence intensity is plotted as a function of samarium oxide concentration, and undoubtedly shows a maximum at the 0.8g of Sm_2O_3. This is the max created from fluorescence intensity versus fluorescence quenching.

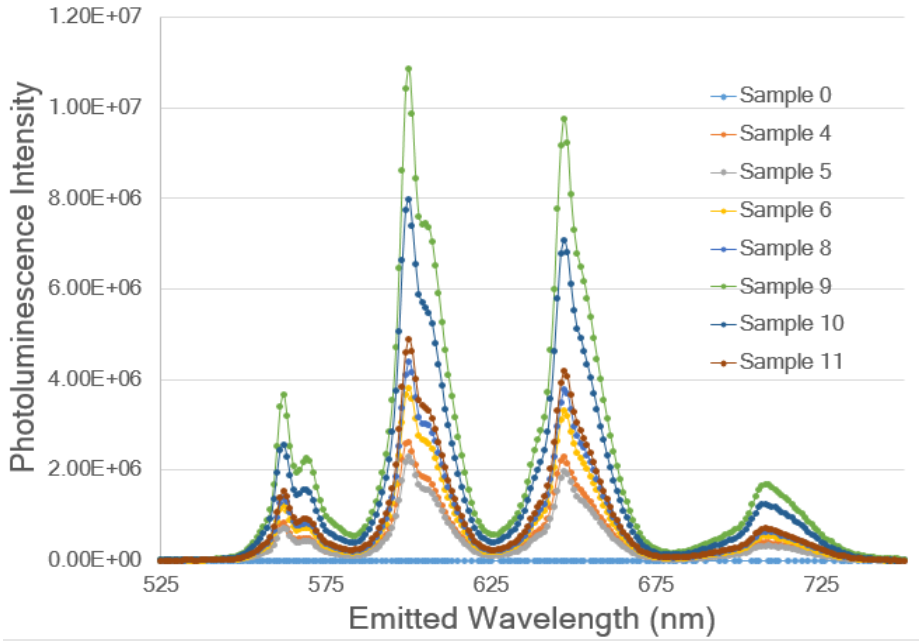


Figure 6: Photoluminescence intensity of samarium oxide concentration range with consistent incident energy.

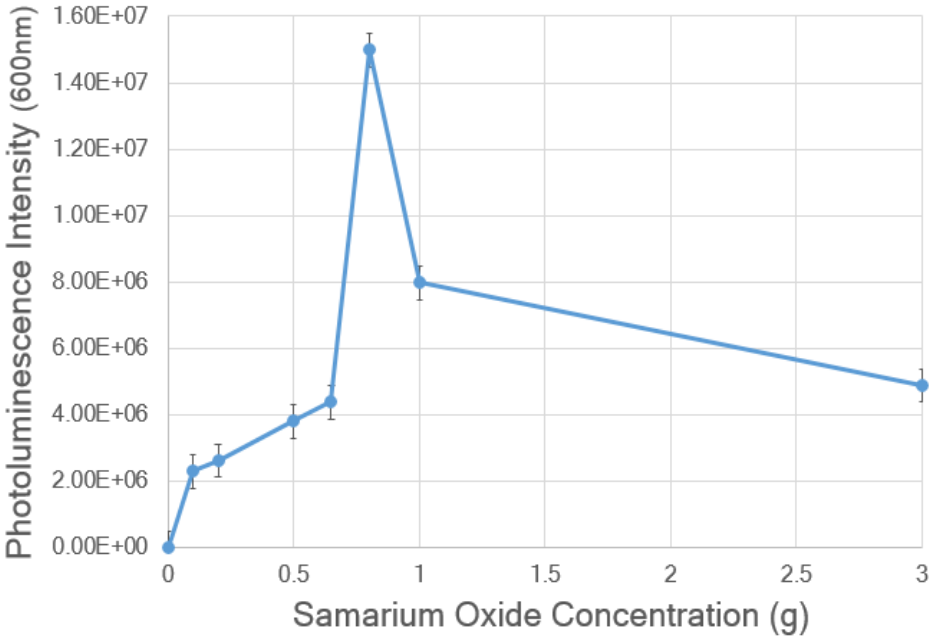


Figure 7: Photoluminescence intensity at 600nm wavelength as a function of samarium oxide composition.

For the practical user, cost is an important factor when choosing a glass composition. Rare earth oxides are expensive compared to transition metal oxides which are usually used to color glass. For example 25g of Sm_2O_3 costs $71.19, when the same amount of CuO costs $19.00.[8,9] On top of this, glass requires much less transition metal oxides to see distinctive change in the color. However artists are always looking at new boundaries to push. Glass artists like to manipulate the optical properties, which fluorescence glass is an extreme in doing so. Table 6 has the compositions and how much each would cost to make a batch of 100g and 2500g. This may seem like expensive batches, but a skilled artist could sell their pieces for much more than the raw materials would cost. This glass could also be used as small accents in larger pieces instead of the whole piece being fluorescent.

Table 6: Cost analysis of compositions containing samarium oxide

	Sm_2O_3 (g)	**100g frit**	**2500g frit**
Composition 0	0.00	$ 0.15	$ 3.86
Composition 4	0.20	$ 0.39	$ 9.84
Composition 5	0.10	$ 0.27	$ 6.85
Composition 6	0.50	$ 0.75	$ 18.80
Composition 8	0.65	$ 0.93	$ 23.29
Composition 9	0.80	$ 1.11	$ 27.77
Composition 10	1.00	$ 1.35	$ 33.75
Composition 11	3.00	$ 3.74	$ 93.53

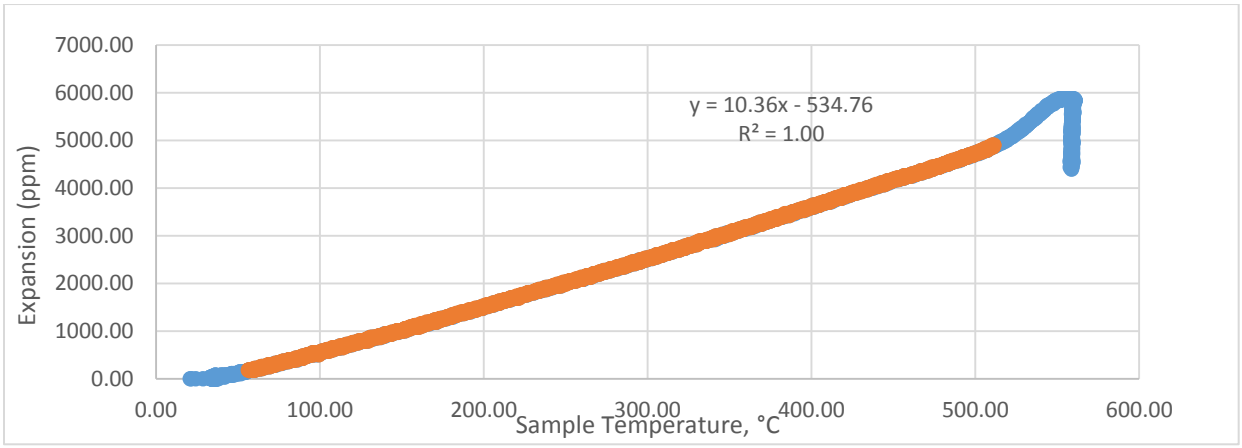
VII. Future Work

Scale up would be the next step. Theoretically there should be no difference in making a 100g batch of composition 9 compared to a 500kg batch of the same composition. However when scaling up new factors can arise. For example 100g batches mix fairly well; however, to create a homogeneous batch of a much larger size extra mixing techniques may be required. This composition would also need to be marketed to the art world. Letting artists know that a glass which fluoresces, and is compatible with their large tank glass, exists is a crucial part in this compositions usefulness.

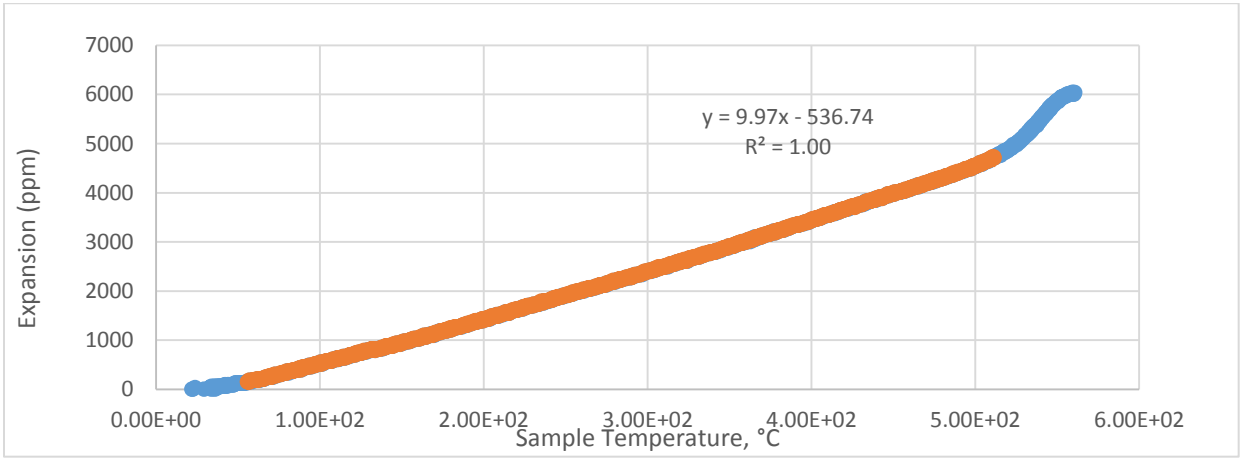
VIII. Conclusion

Artists are always looking for a new way to depict concepts. Fluorescent glass is not commonly used due to its lack of availability and general knowledge. Composition 9, which is 0.8g of samarium oxide to 100g of System 96 frit, is the optimal composition created. Composition 9 is compatible with System 96 in terms of thermal expansion. This composition is also has the highest fluorescence intensity of the compositions tested. The price may seem high, but the fluorescence effect goes a long way in making a statement. In the end composition 9 should be scaled up and used by artists.

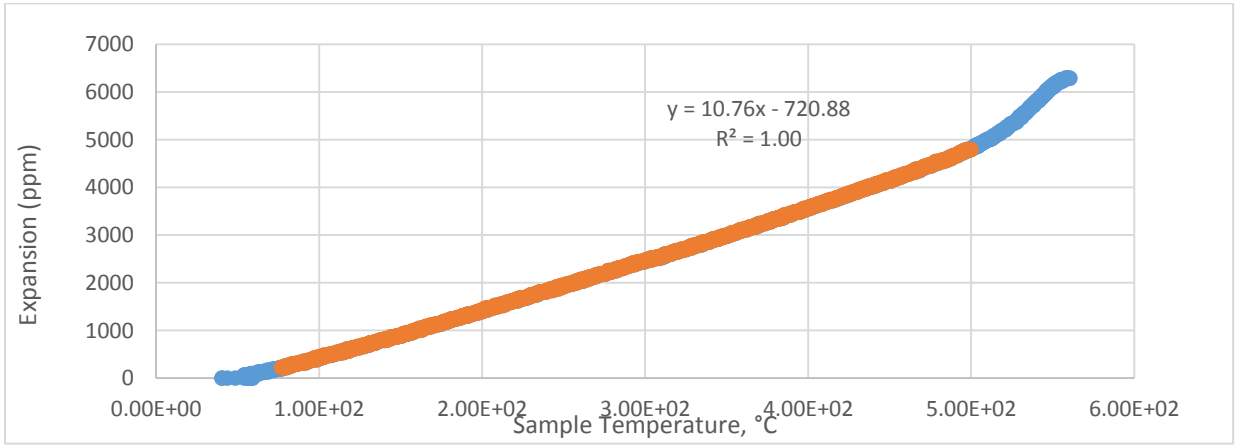
IX. Appendix: Dilatometer Data



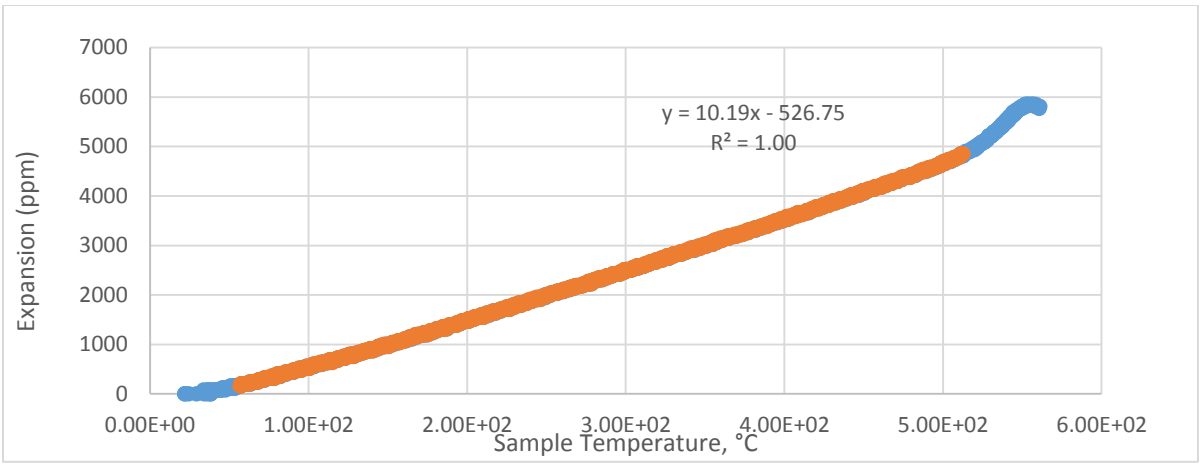
A-1: Composition 0 dilatometer data



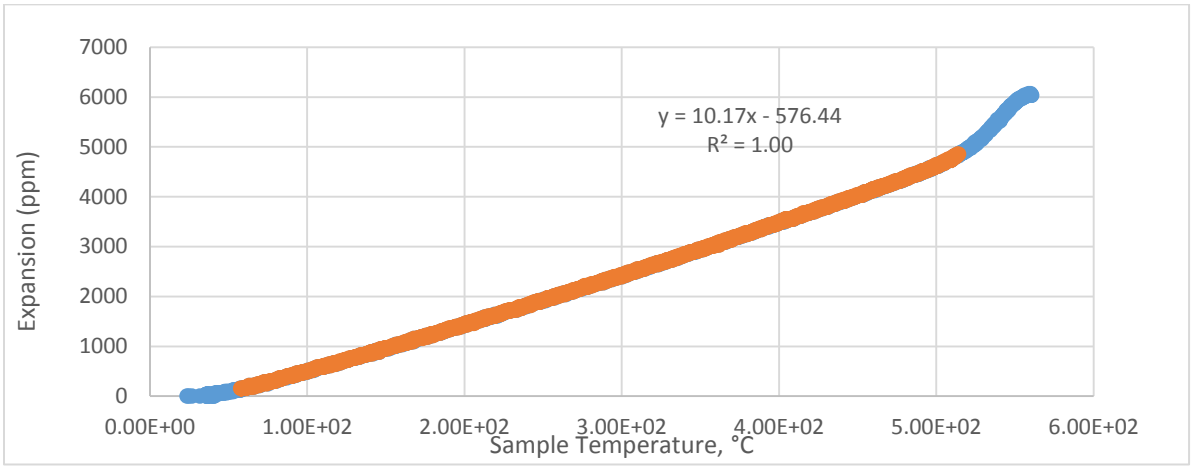
A-2: Composition 4 dilatometer data



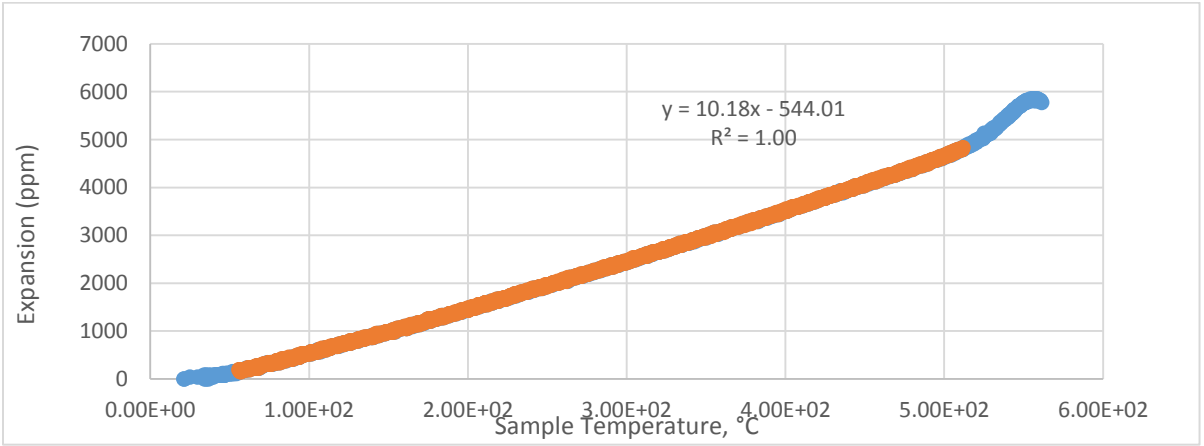
A-3: Composition 5 dilatometer data



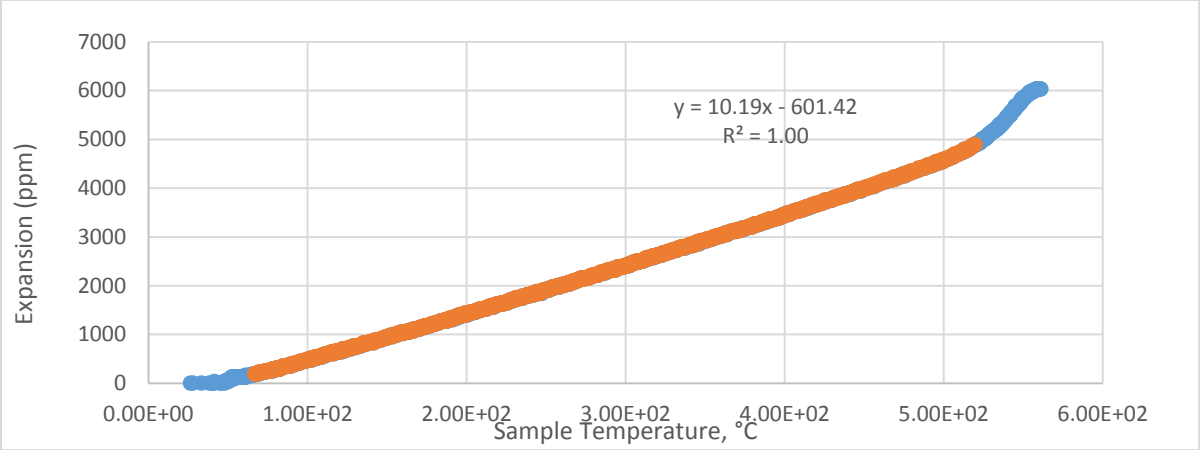
A-4: Composition 6 dilatometer data



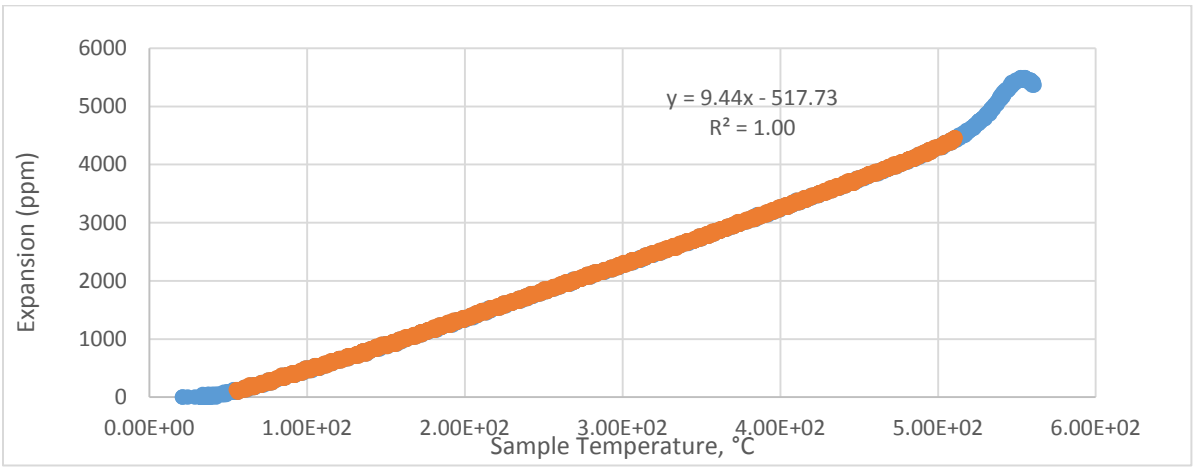
A-5: Composition 8 dilatometer data



A-6: Composition 9 dilatometer data



A-7: Composition 10 dilatometer data



A-8: Composition 11 dilatometer data

X. References

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