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Abstract

As the project approaches the end of the first year, the materials screening components of the work are ahead of schedule, while all other tasks are on schedule. For solid oxide fuel cells (SOFC), a series of 16 sealing glasses have been prepared and characterized. Traditional melting was used to prepare all of the glasses, and the sol-gel approach has been used to prepare some of the glasses as well as other compositions that might be viable because of the low processing temperatures afforded by the sol-gel method. The glass characterization included measurements of the viscosity and thermal expansion of the glasses, as well as the thermal expansion of the partly crystalline glass ceramics. In addition, the wetting and sintering behavior of all glasses has been measured, as well as the crystallization behavior. The time and temperature at which crystalline phases form from the glasses has been determined for all of the glasses. Each glass ceramic contains at least two crystalline phases, and most of the crystalline phases have been positively identified. Room temperature leak testing has been completed for all sealants, and experiments are in progress to determine the DC electrochemical degradation and degradation in wet hydrogen.

The second component of the work, focused on seals for higher-temperature discharge lighting, has focused on determining the phase relations in the yttria – alumina – silica system at various silica levels. Again, traditional melting and sol-gel synthesis have been employed, and the sol-gel method was successful for preparing new phases that were discovered during the work. High temperature diffraction and annealing studies have clarified the phase relations for the samples studied, although additional work remains. Four new phases have been identified and synthesized in pure form, from which full structure solutions were obtained as well as the anisotropic thermal expansion for each phase. Functional testing of lamps are on on-going and will be analyzed during year 2 of the contract.

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1 Introduction

The focus of the project is sealing materials for solid oxide fuel cells and discharge lighting. In both cases, energy efficiency is the ultimate goal, and the technologies are rapidly evolving. The sealing materials in both cases are glass-ceramics, which afford the processing efficiency of a glass with the thermal, mechanical, chemical, and electrical stability of a crystalline material.

In the case of SOFC applications, the team has identified key performance parameters that include:

- Gas tight (<1% allowable leakage) at 800 °C in both oxidizing and reducing atmospheres over the life of the fuel cell (50,000 hours).
- Accommodate stresses generated due to potential CTE mismatches through hundreds of thermal cycles.
- Low processing temperature (<900 °C) allowing for the use of low cost interconnect materials.
- Must not contain volatile components or chemically react (i.e., poison) with other stack components over life, thus ensuring performance of cell active layers.
- Must be electrically insulating and stable under load to avoid shorts in the stack.
- Must be low cost.

For lighting applications, where the operating temperature is significantly higher, the critical parameters include:

- Shorter arc gap for light collection efficiency
- Better spectral distribution/ color efficiency
- High Temperature/Pressure
- Long-life / Reliability

The project plan includes design, synthesis, characterization, and device testing for both systems. Traditional synthesis and sol-gel synthesis are both included in the work, because a breakthrough technology might be found by using the sol-gel approach. Figure 1 shows a flowchart of the project activities for each system.

Figure 1: Overview of project activities for lighting and fuel cell sealing materials.

2 Executive Summary

Glass ceramic sealants for solid oxide fuel cells (SOFC) and discharge lamps have been investigated. In the case of the SOFC application, a series of 13 glasses were prepared as part of a statistical experimental design with the goal of obtaining new sealants that have a thermal expansion coefficient (TEC) matching the other SOFC components and longer life as a result of better tolerance for wet hydrogen during fuel cell operation. The primary compositional goal was to reduce the boron content of the glasses while maintaining TEC matching with the fuel cell components and the flow characteristics so that practical seals can be manufactured. Boron stability in wet hydrogen is known to be a problem, and as such may compromise the integrity of the seal.

All 13 glasses were prepared using conventional melting and characterized to determine the viscosity, crystallization behavior, bulk TEC after crystallization, wetting and sintering. An additional series of 5 samples that were compositionally optimized after the initial screening were also prepared and characterized. All of the SOFC glasses are being compared to the original base glass composition used by GE and the newer, state-of-the-art glass developed by the Pacific Northwest National Laboratory (PNNL). The PNNL glass, identified as "G18" is a composition that was recently developed and published [1].

The designed glasses met the initial target viscosity and TEC matching criteria, and were therefore subjected to wetting and sintering tests to evaluate their behavior in powder form. Several of the designed glasses did not flow and/or sinter well when processed in powder form, but several of the glasses had appropriate wetting and sintering behavior. Based on GE's sealing test vehicle, improvements to the wetting characteristics of the more refractory Alfred glasses could be achieved by increasing the load during sealing. Six glasses were downselected and prepared by a contract vendor, and a significant effort was undertaken to evaluate the performance of the vendor-melted glasses. Unfortunately, the vendor was not successful in producing the glasses at the target compositions, so additional glasses were melted at Alfred University.

Several of the new sealants have passed the leak testing criteria at room temperature, and several test vehicles are currently undergoing extended degradation testing under wet hydrogen and air at 800°C. Additionally, electrochemical degradation tests are underway using DC electric fields.

In addition to the traditional glass melting process, the sol-gel method has been investigated as a means of producing sealants that can be processed at low temperatures but still provide the requisite TEC matching and improved durability. The sol-gel component of the work has thus far not yielded sealants that are competitive, but further work is underway that might lead to a breakthrough technology. The sol-gel work is planned to continue through May, 2005.

The success of the project to date provides great confidence that new, optimized sealants will result from the work. The detailed composition-property matrix that has been developed provides the foundation for further materials optimization.

Lighting seals are also under study and have been produced via traditional melting and the sol-gel approach. The rare earth – alumina – silica system is under study because of the known high melting temperatures and resistance to chemical attack. Unfortunately, very little information was known about the phases that form in the system, the stability ranges of the phases, and the TEC for each phase. Extensive high temperature X-ray diffraction and annealing studies, complemented with electron backscattered diffraction and microprobe analysis, were

undertaken. At this point, the entire equilibrium phase diagram in the regions of interest has been developed. Four new phases have been isolated and identified, and their crystallographic structures solved. In addition, the anisotropic thermal expansion for each new phase has been measured. The TEC for the three target bulk sealants has been measured up to 1400°C, providing another design parameter. Some wetting experiments remain to be completed, as well as viscosity measurements of the bulk sealants. In-lamp testing, scheduled to begin at the start of year two, are currently in the planning stage.

3 Experimental

3.1 Traditional Synthesis

3.1.1 Solid oxide fuel cell sealants

Using the existing technology as a baseline, multiple glass compositions were identified using the D-Optimal design process. 14 oxide glass modifier components were identified as candidate property modifiers and glass preparation was begun.

The glasses were prepared from reagent grade raw materials and melted in a platinum crucible at 1400°C for 1 h. The glass melts were poured into a steel mold and annealed from 680°C to room temperature in 12 h.

The thirteen initial SOFC sealing glasses allowed quantification of the influence of twelve components on the desired properties. Over the course of the budget year, initial data indicated that additional compositions might improve the behavior of the sealing glasses. Therefore, an additional series of glasses was prepared, totaling 10 additional glasses. One of the 10 was the composition published by the Pacific Northwest National Laboratory and commonly known in the literature as “PNNL G18.”[1].

Some of the cast glass was characterized for viscosity and TEC, in the amorphous state, and some was milled to form a powder for all other experiments. Each glass was crushed and milled in propanol using a McCrone micronizing mill with Al₂O₃ elements. The resulting powders were sorted and characterized for particle size distribution and then used in all subsequent experiments.

3.1.2 Lighting sealants

Sealing materials for lighting applications have also been identified using an approach that is similar to that used for the SOFC sealants. The Y₂O₃-Al₂O₃-SiO₂ system with various levels of silica additions in the yttrium aluminum garnet portion of the ternary phase diagram has been targeted.

The synthesis method involved melting at ~1800°C in Mo containers under wet hydrogen, followed by quenching to produce monolithic glass castings. The glass castings were cut and ground to powder for all tests.

3.2 Sol-gel synthesis

The sol-gel approach was used for both lighting and SOFC applications. To date, five different synthesis procedures have been used or developed, which are summarized below.

Process A

Aluminum sec-butoxide dissolved in warm formic acid solution. Tetraethyl orthosilicate added with stirring; yttrium oxide powder added slowly with heating and stirring. Dilute ammonium hydroxide added dropwise to yield product; dried at 70-80°C in air.

Process B

Yttrium oxide dissolved in warm nitric acid solution. Tetraethyl orthosilicate added with stirring; aluminum sec-butoxide added with heating and stirring. Dilute ammonium hydroxide added dropwise to yield product; dried at 70-80°C in air.

Process C

Yttrium oxide dissolved in warm nitric acid solution. Tetraethyl orthosilicate added with stirring; aluminum nitrate added with heating and stirring. Dilute ammonium hydroxide added dropwise to yield product; dried at 70-80°C in air.

Process D

Lanthanum oxide powder refluxed in hot acetic acid. Solution is allowed to cool slightly, TEOS added with gentle stirring. Barium acetate powder added with heating and stirring. Solution is allowed to gel.

Process E

Tetraethyl orthosilicate added to warm nitric acid solution with stirring. Aluminum nitrate added with stirring at approximately 40°C; allowed to dissolve. Boric acid (if appropriate), strontium acetate, barium acetate added with stirring and allowed to dissolve. Solution permitted to cool; dilute ammonium hydroxide added dropwise to yield product. Dried at 70-80°C in air.

3.3 Chemical behavior: X-ray diffraction, microscopy, and wetting angle behavior

A custom high temperature furnace, described by Misture [2] was mounted on a Siemens D500 diffractometer for the high temperature x-ray diffraction (HTXRD) measurements. The HTXRD measurements were made using Co or Cu radiation and a Braun position-sensitive detector that was scanned over an appropriate angular range to measure the peaks of interest.

The measurements were made under static air (breathable quality) or under a mixture of He/4%H₂, depending on the experiment. All heating rates were 60 K/min unless indicated otherwise.

All of the HTXRD measurements were made under isothermal conditions, that is, the specimen was heated to the target temperature and held at the target temperature during the XRD measurement. XRD patterns were always collected at room temperature both before heating the specimen and then after cooling.

The specimens were prepared by lightly grinding the monolithic part in an alumina mortar and pestle under ethanol, and then the HTXRD specimen was prepared as a thin layer of powder (approximately 50 µm thick) by dripping the powder/ethanol slurry onto the sample holder. The sample holder employed was a single-crystal sapphire disk cut so that it does not contribute any diffraction peaks to the XRD pattern, which was in turn supported by a sapphire plate. Some of the HTXRD measurements were made of the sealing glasses directly in contact with the YSZ side of the bilayer or alternately in contact with the NiO side of the bilayer.

Room temperature diffraction was performed on a standard Siemens D500 diffractometer that employed Cu radiation.

Scanning electron microscopy was performed in both backscatter and secondary electron mode, and electron backscattered diffraction was also performed. Several SEM instruments were used in the analyses, including an Amray 1810, a Philips 515 and an ETEC autoscan.

Extensive measurements were performed to evaluate the wetting behavior of sealing glasses in contact with the SOFC components. The study addresses not only the fundamental science of wetting and reactivity but also has implications in predicting the gap filling behavior of the sealants.

Experiments were carried out using an automated high temperature optical microscope Misura 3, manufactured by Expert Systems Srl, Modena, Italy that provides the contact angle and sample height as a function of temperature at any controlled heating and cooling rate. Two distinct experiment sets were performed that included the sealing glass in its pure form and then the sealant glass with added fillers that are potentially important for gap filling to meet the hermeticity requirements.

A total of 48 material combinations were tested with variations as follows:

- Four substrate conditions, including: the zirconia side of the fuel cell bilayer, the as-manufactured metal interconnect surface, the preoxidized metal interconnect surface, and finally one modified metal surface.
- Two different filler materials with two particle size distributions each
- Four different filler loadings.

3.4 Thermal behavior: Thermal expansion, viscosity

The viscosity was measured over the range of $\log(\eta/\text{Pa}\cdot\text{s}) = 5.5 - 9.5$ using a Theta model "Rheotronic R" parallel plate viscometer. The viscometer was calibrated with NIST standard SRM 710A. The glass samples were cylinders (9 mm diameter, 6 mm height) with parallel flat smoothened faces. The measurements were made according to a procedure described in [9]. The heating rate was 1 K/min.

The CTE and true expansivity were determined by a differential dilatometer, calibrated with standards for platinum (ASTM E 228 - 95), polycrystalline alumina, and fused silica (NIST SRM 739). The heating rate was 4 K/min. The sample dimension was a rod (length 25.4 mm), with square cross-sectional area (thickness ~6 mm).

3.5 Electrical conductivity

A direct current (DC) conductivity test is currently being implemented at GE Research in order to study the effect of electric potential on seal glass stability. The seal used in fuel cells needs to be electrically insulating and stable under stack voltage potentials (i.e., no ionic conduction of seal components) to avoid an electrical short in the stack. The tests are conducted at 800°C, in air, using a constant 1V potential. In the single sample set-up, the current is monitored as a function of time using a data logger. GE is in the process of implementing a multi-sample test to expedite screening of various seal glasses (see Figure 2).

Figure 2: Schematic of multi-sample set-up at GE Research.

To determine if glass polarization occurs under DC fields, the GE Research Center performed impedance spectroscopy measurements in order to determine the ionic and electronic conductivity of the sealant as a function of temperature. Bulk glass and glass-ceramic specimens of the baseline sealant were prepared. The samples were rectangular in shape of length 2.6 cm with a square cross section of area 0.107cm^2 . The samples were instrumented with 2 gold wires on each square end, held in place with gold paste covering the entire square on each end. The samples were taken to 4 measurement temperatures of 400, 500, 550 and 600°C . At each of these temperatures a 4-point AC impedance measurement was taken between 1MHz and 0.03Hz. At each of these temperatures the samples showed that they were out of the 100Mohm measurement limit of the equipment. The bars have been re-submitted for measurement across the 3 mm thickness. If the resistance still exceeds the limits of the equipment then the sample will be next sliced to a $\frac{1}{2}$ mm thickness.

3.6 Leak testing & seal evaluation

In previous work, a simple test vehicle was defined and has been used at the GE Global Research Center to screen various sealant materials (see Figure 3). The test vehicle allows us to quickly evaluate key properties of the sealant including wetting characteristics, CTE mismatch, chemical compatibility with other components, and integrity of the seal joint (i.e. gas tightness or hermeticity). The RT leakage rate of the sealed system is measured by monitoring the pressure increase in a known chamber volume over time at various differential pressures using air or helium gas. The lower measuring range of the equipment is approximately 10^{-4} cc/sec, which was established through gage R&R studies. This range was determined to be sufficient based on system specifications for allowable leakage rates. One major limitation, however, is that it is only a RT measurement technique. Of ultimate interest is the leakage rate of sealant materials as a function of temperature (i.e. 800°C) as we suspect that some materials will improve or degrade as a function of temperature/time. The Research Center is in the process of developing in-house techniques, under another program, to support this activity.

Figure 3: Test vehicle used at GE Global Research Center for screening various seal materials.

3.7 Degradation studies for SOFC sealants

Functional testing plans include evaluating the chemical stability of the sealant at 800C (nominal operating temperature) over time in various *simulated* fuel cell environments (i.e. air, wet H₂). Also planned are thermal cycle tests as the sealant must maintain mechanical integrity during fuel cell start-up and shut down processes. Leakage rate degradation, as well as in-depth microstructure analysis, will be monitored and used to help determine potential limitations of various sealant materials. Such testing is already underway on the baseline sealant material.

3.8 Lamp life testing

Preliminary functional lamp testing has been conducted and will continue through year 2 of the contract. Analyses of the lamps are on-going and will be described in the final report.

4. Results and Discussion

4.1. Synthesize Initial Candidate Systems

4.1.1. Conventional synthesis of SOFC sealants

No problems were encountered during the synthesis, and none of the target glasses crystallized during casting. All samples formed crystal-free glasses.

4.1.2. Conventional synthesis of lighting sealants

Seven specimens in the compositional range Y₂O₃-Al₂O₃-SiO₂ at low SiO₂ content were synthesized at GE and were characterized as a team effort. No synthesis problems were noted after repeated synthesis. The phases present after synthesis are described below in the context of the phase equilibria work.

4.1.3. Sol-Gel Synthesis for Lamp Applications

The literature survey for sol-gel approaches to sealing glasses for high temperature lamps was completed by the graduate student. The first phase of this study focused on choosing the appropriate precursor materials for producing amorphous gels, and the procedures described in section 3 have been successful to date.

A dual approach has been taken in the sol-gel work to achieve the following:

- i. an optimized composition, especially related to the low-temperature processing afforded by the sol-gel process, for sealing lamps and fuel cells
- ii. as an aid in synthesis and identification of previously unknown phases that were encountered in the studies of the SOFC and lighting sealants produced by traditional melting. This point is of critical importance because of the complexity of the phase relations in the systems under study.

Table 1 summarizes the work completed to date, with detailed analysis following.

Table 1: Summary of sol-gel work related to lighting seals.

Sample Designation*	Process	Phases Present	Heat Treatment	Remarks
YA	A	$\text{YAlO}_3 + \text{Y}_2\text{Al}_4\text{O}_9 + \text{Y}_3\text{Al}_5\text{O}_{12}$	1100°C - 5h	Al deficient by ICP. To be repeated.
YA	B	$\text{YAlO}_3 + \text{Y}_2\text{O}_3 + \text{Y}_3\text{Al}_5\text{O}_{12} + \text{Y}_4\text{Al}_2\text{O}_9$	1100°C - 5h	
YA	C	To be determined	1100°C - 5h	
YAS-1	A	$\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{Y}_2\text{Si}_2\text{O}_7$	1100°C - 5h	Al deficient by ICP. To be repeated.
YAS-1	B	$\text{YAlO}_3 + \text{Y}_3\text{Al}_5\text{O}_{12}$	1100°C - 5h	
YAS-1	C	To be determined	1100°C - 5h	
YAS-3	A	$\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{Y}_2\text{Si}_2\text{O}_7$	1100°C - 5h	Al deficient by ICP. To be repeated.
YAS-3	B	$\text{Y}_2\text{O}_3 + \text{Y}_4\text{Al}_2\text{O}_9$	1100°C - 5h	
YAS-3	C	To be determined	1100°C - 5h	
$\text{Y}_2\text{Si}_2\text{O}_7$	C	$\text{Y}_2\text{SiO}_5 + \text{SiO}_2$	1100°C - 20h	
$\text{Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	C	$\alpha\text{-Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	1100°C - 20h	
$\text{Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	C	$\beta\text{-Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	1300°C - 10h	
$2\text{Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	C	To be determined	1100°C - 20h	In progress.
$2\text{Y}_2\text{Si}_2\text{O}_7 + \text{SiO}_2$	C	To be determined	1300°C - 10h	In progress.
$\text{Y}_{4.67}\text{Si}_3\text{O}_{13}$	C	To be determined	1100°C - 20h	In progress.

*yttrium aluminate (YA) and yttrium aluminosilicate (YAS). The YAS codes of 1, 2, 3, etc. are used throughout the document.

To date, yttrium aluminate (YA) and yttrium aluminosilicate (YAS) glasses have been successfully prepared. In addition, attempts have been made to produce a $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) precursor.

The low-silica yttrium aluminosilicate was found to contain $\text{Y}_3\text{Al}_5\text{O}_{12}$ and hexagonal YAlO_3 phases after heat-treatment to 1000°C for 1 hour and slow-cooling to room temperature. The YAlO_3 phase was identified to be a high-temperature polymorph, suggesting that the sol-gel derived process stabilizes the high-temperature phase. This material will be further treated to 1100°C and further characterized. Figure 4 shows the X-ray diffraction pattern for this composition.

Figure 4: X-ray diffraction pattern for the low-silica ternary yttrium aluminosilicate composition following heat treatment to 1000°C for 1 hour.

The high-silica yttrium aluminosilicate was found to contain Y_2O_3 and $Y_4Al_2O_9$ phases after heat-treatment to 1000°C for 1 hour. Figure 5 shows the X-ray diffraction pattern for this composition. This material will be similarly treated to 1100°C and further characterized.

Figure 5: X-ray diffraction pattern for the high-silica ternary yttrium aluminosilicate composition following heat treatment to 1000°C for 1 hour.

Figure 6 shows the result of the preparation of the pure YAG composition after heat treating to 1000°C for 1 hour. X-ray diffraction as shown in Figure 6 identified the phases present as

$\text{Y}_4\text{Al}_2\text{O}_9$, $\text{Y}_3\text{Al}_5\text{O}_{12}$, Y_2O_3 , and YAlO_3 . Heat-treatment to 1100°C reportedly produces phase-pure YAG; this heat-treatment will be carried out in an attempt to reproduce these results prior to the addition of silica to the composition.

Figure 6: X-ray diffraction pattern from a pure YAG composition following heat treatment to 1000°C for 1 hour.

The second set of sol-gel synthesis attempts were carried out to aid identification of phases discovered in the YAS sealants. Both $\alpha\text{-Y}_2\text{Si}_2\text{O}_7$ and $\beta\text{-Y}_2\text{Si}_2\text{O}_7$ have been formed by the sol-gel process through the addition of excess silica. Full characterization of the phases, including structure solutions and anisotropic TEC measurements, has been completed, and is reported in section 4.12.

4.1.4. Sol-Gel Synthesis for SOFC Applications

The barium lanthanum silicate (BLS) glasses were selected as possible candidate sealing materials. Glasses in the general composition range of 30-35 mole% BaO , 10-15 mole% La_2O_3 , and 50-60 mole% silica will be investigated since they seem compatible with several critical parameters, including thermal expansion coefficient (10-12 ppm) and softening temperature ($750\text{-}850^\circ\text{C}$). Again, the choice of precursor materials is critical to successful sol-gel processing. Table 2 summarizes the activities to date.

Table 2: Summary of sol-gel synthesis for SOFC applications.

Sample Designation*	Process	Phases Present	Heat Treatment	Remarks
LBS-A	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
LBS-C	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
LBS-D	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
LBS-E	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
LBS-F	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
LBS-G	A	Uncharacterized	Simulated seal cycle	No softening/adhesion
AU #35 - 0 B2O3	B	Barium strontium nitrate + amorphous material	To undergo simulated sealing cycle	In progress
AU #35 - 3 B2O3	B	Barium strontium nitrate + amorphous material	To undergo simulated sealing cycle	In progress
AU #35 - 6 B2O3	B	Barium strontium nitrate + amorphous material	To undergo simulated sealing cycle	In progress

* LBS indicates La Ba silicate, and the AU#35 is one of the designed glass compositions.

A series of four sol-gel-derived glasses composed of varying proportions of BaO, La₂O₃, and SiO₂ have been prepared. X-ray diffraction revealed the as-synthesized samples to be largely amorphous, as shown in Figure 7. Further characterization of this series of glasses is in progress, and will include thermogravimetric analysis (TGA) and simulated sealing cycles. Decreases in the silica content are expected to result in more favorable softening characteristics. A system is currently being devised to perform reproducible sealing experiments with the sol-gel derived glasses.

Figure 7: X-ray diffraction results for the sol-gel derived glasses. Silica content increases going down the series.

Rapid screening experiments for the sol-gel glasses has been started, but is not yet completed. The screening includes sandwiching a pellet of the sol-gel precursor between bilayers and heat treating. To date, no softening of the pellet or adhesion to the substrates has been noted with any of the compositions tested. Additional work is planned.

Finally, the synthesis of a glass composition similar to the Alfred #35 glass has been carried out by a sol-gel process. Boron oxide has been replaced with silica in an effort to increase the chemical durability of the glass. The thermochemical properties and sintering behavior of the boron-free version of the Alfred #35 glass will be assessed using HTXRD and simulated sealing tests.

4.2. Viscosity of SOFC glasses before crystallization

The results of the viscosity measurements to date are shown in Figure 8 and Table 3. Overall, the glasses prepared to date were found to be satisfactory for the needed rheological behavior. Glass 24 crystallized during the viscosity measurement starting at about 840°C, and therefore composition 24 will probably not be applicable for sealing at 900°C.

The results demonstrate that ZrO_2 increased the viscosity more strongly than Al_2O_3 . The transition metal oxides, P_2O_5 , and BaO did not influence the viscosity significantly, and B_2O_3 decreased the viscosity, as expected.

Table 3: Temperatures of constant viscosity (isokom) and CTE.

#	Isokom temperatures in °C				CTE (200-500°C) in ppm/K
	$\log(\eta/\text{Pa}\cdot\text{s}) = 6$	$\log(\eta/\text{Pa}\cdot\text{s}) = 7$	$\log(\eta/\text{Pa}\cdot\text{s}) = 8$	$\log(\eta/\text{Pa}\cdot\text{s}) = 9$	
13	857.3	822.0	790.8	763.1	10.81
14	837.3	803.1	772.6	745.2	11.05
15	856.5	820.8	789.2	761.2	11.04
16	869.5	834.4	803.0	774.8	10.82
17	867.0	833.7	803.3	775.6	10.87
18	880.9	845.9	815.2	788.0	10.68
19	857.8	823.4	792.3	764.0	11.16
20	859.5	824.8	793.9	766.3	11.15
21	in progress				11.11
22	in progress				
23	in progress				10.89
24	Crystallization		805.4	776.8	10.82
25	in progress

Figure 8: Viscosity curves of the glasses prepared to date.

4.3. Phase evolution, wetting, and characterization of SOFC sealants

After obtaining preliminary crystallization and viscosity data, a downselection of the designed glass compositions was performed and the glasses were melted by a contract laboratory. The reason for having a vendor prepare the glasses was to supply a large quantity of glass so that GE could carry out the required functional testing. After receiving the glass from the vendor, several screening experiments were performed to confirm the behavior of the glasses. Unfortunately, as described in detail below, the vendor did not reach the correct glass composition, and the behavior of the glasses was significantly different than those melted at Alfred University.

Section 4.3.5 includes a summary of all glasses melted to date in terms of phase evolution and wetting – and should be considered a brief overview. The following section, 4.4, includes all of the room temperature XRD, HTXRD, and wetting studies performed on the glasses melted at Alfred and the vendor melted glasses. Unless explicitly specified, all glasses were melted at Alfred University.

4.3.5. Overview of wetting and sintering

The variation in contact angle and sample height of SOFC sealing glasses melted at Alfred University was measured using hot-state microscopy (HSM) on alumina substrates for a global comparison of the sealants. The use of alumina was justified because none of the sealants showed significant deformation. Additional experiments, shown below, included measurements of the sealants in contact with the various SOFC components. Table 4 shows the high temperature microscope images for all the glasses, and Figure 9 shows the variation in contact angle with temperature. Figure 10 shows the variation in sample height with temperature. Glasses 13 to 18 soften below 900°C, while glasses 19 to 24 do not soften below 1000°C.

From the data, it is clear that some of the sealing glasses do not deform without an applied load at temperatures below ~900°C. The target sealing temperature for the SOFC stacks is 900°C,

therefore we expect that the flow properties of glasses 19-24 will be unsuitable because the sealant must, at a minimum, flow to fill surface imperfections in the components. While the lack of deformation does not by itself preclude the possibility of adhesion and sealing, the sintering and wetting behavior are reliable screening tests.

Table 4: Images of sealing glass pellets on alumina substrate at various stages of the heating cycle.

Glass 13	Glass 14	Glass 15	Glass 16
25°C	25°C	25°C	25°C
777°C, 90°, 95%	749°C, 86°, 95%	762°C, 88°, 95%	775°C, 86°, 95%
900°C, 108°, 77%	900°C, 115°, 73%	900°C, 114°, 70%	900°C, 120°, 75%
1000°C, 109°, 76%	1000°C, 103°, 71%	1000°C, 117°, 70%	1000°C, 119°, 74%

Glass 17	Glass 18	Glass 19	Glass 20
25°C	25°C	25°C	25°C
772°C, 82°, 95%	789°C, 87°, 95%	773°C, 88°, 95%	768°C, 89°, 95%

900°C, 115°, 70%	900°C, 104°, 77%	900°C, 86°, 80%	900°C, 86°, 77%
1000°C, 115°, 66%	1000°C, 107°, 75%	1000°C, 92°, 79%	1000°C, 86°, 70%

Glass 21	Glass 23	Glass 24
25°C	25°C	25°C
763°C, 88°, 95%	786°C, 85°, 95%	778°C, 83°, 95%
900°C, 84°, 83%	900°C, 84°, 78%	900°C, 86°, 84%
1000°C, 86°, 78%	1000°C, 87°, 78%	1000°C, 88°, 83%

Alfred-melted G18	Glass 26	Glass 33

25°C	25°C	25°C
703°C, 89°, 95%	776°C, 88°, 94%	756°C, 83°, 95%
843°C, 103°, 51%	876°C, 95°, 75%
898°C, 85°, 37%	901°C, 101°, 75%	901°C, 118°, 73%
998°C, 20°, 11%	996°C, 98°, 74%	1001°C, 114°, 73%
		1056°C, 76°, 61%
		1061°C, 66°, 32%
		1095°C, 20°, 13%

Figure 9: Variation in contact angle with temperature of sealing glasses.

Figure 10: Variation in sample height with temperature of sealing glasses on alumina substrates.

4.3.6. Overview of phase formation

Each glass was heat treated using the target sealing cycle that involves heating to 900°C. The goal is to produce a glass-ceramic by partial crystallization of the sealing glass during heating, during an isothermal hold at the maximum temperature, or during cooling. Ideally, the glass should crystallize during the isothermal hold or during cooling, in which case it is possible to

easily control the crystalline fraction and rate of crystallization. Crystallization during heating is less desirable, because it is difficult to control the extent and rate of crystallization.

Extensive X-ray diffraction was performed for each glass-ceramic sample after the sealing cycle. Powdered samples of the glasses were pressed into pellets and fired at 900°C for 12 hours. Pellets were milled in a McCrone micronizing mill and analyzed using X-ray diffraction.

In general, several phases were common to most of the samples, however, full identification of the crystalline products was not possible. Future work is planned to attempt to identify all of the crystalline phases present in the downselected sealants. Figure 11 shows a series of XRD patterns with the similar XRD patterns grouped together. Detailed phase identification including Rietveld full pattern fitting is shown for each glass in section 4.4.

Figure 11: X-ray diffraction patterns for each glass after being subjected to the target sealing profile. The vertical boxes indicate the groupings of XRD patterns that are similar. Full phase identification for each specimen is included in section 4.4.

High temperature XRD was used to monitor the growth of the crystalline phases from the base sealing material as a function of temperature and substrate. A previously unidentified oxide phase was discovered containing Ba, Mg, and Si, and the crystal structure was solved and refined using room temperature diffraction. In addition, the crystallographic thermal expansion was determined out to 1200°C using high temperature XRD.

Table 5 gives a summary of the crystallization onset temperatures for each glass. Note that all of the glasses were measured as powders, and therefore surface nucleation is expected. In addition, it is clear from the HTXRD results in table 1 that all of the glasses crystallize on heating, with onset temperatures of 850 or 900 °C.

Table 5: Temperatures at which the presence of a crystalline phase was first observed in SOFC sealing glasses during HTXRD analysis.

Glass	First Crystallization	Phases present* after 900°C heat treatment
13	850°C	B, LQ, T
14	850°C	U
15	850°C	B, HC, LC, T
16	900°C	U
17	900°C	B, HC, T
18	900°C	B, LQ, T
19	850°C	Not Measured
20	850°C	B, LQ, C, T
21	800°C	U
23	900°C	B, HC, LC, T
24	850°C	Not Measured
26	900°C	B, T
33	850°C	U
35	800°C	U
G18	850°C	U

*B = $\text{BaAl}_2\text{Si}_2\text{O}_8$

T = unidentified triclinic phase with lattice constants $\sim 6.66 \times 4.20 \times 6.11 \text{ \AA}$, $80^\circ \times 62^\circ \times 77^\circ$. Note that the unit cell determination for this phase is questionable, and the composition and structure is unknown.

U = Unidentified phase or phases present, but not all unidentified phase(s) are the same.

LC = Low Cristobalite

HC = High Cristobalite

LQ = Low Quartz

4.4. Detailed investigation of crystallization, wetting, and comparison of vendor-melted and Alfred-melted glasses.

A full study including HTXRD, ambient temperature XRD, and wetting has been completed for all of the original designed glasses and the additional optimized glasses. The results are summarized in the previous sections, and the details are provided below.

4.4.1. Bulk chemical analysis of the glasses melted at Alfred and those melted by a contract vendor.

Figure 12 shows the results of an inductively coupled plasma atomic emission analysis of the bulk chemistry of six glasses melted at Alfred University and six glasses melted by a contract

Figure 12: Compositional differences from the target values for six of the glasses melted at Alfred University (top) and six melted by a contract vendor(bottom).

vendor. The glasses melted at Alfred are all within 1% of the target composition, while those melted by the vendor differ in the Ba and Si content by as much as 3.5%. The inaccuracy of the compositions melted by the vendor have a major impact on melting and wetting behavior, as shown below.

4.4.2. Detailed results for each sealing glass

Glass 13

Figure 1.1 shows deviation from the target composition of Alfred-melted and vendor-melted glasses. Data was received from GE Research. Alfred-melted glass 13 is within 1 mole % of the target composition. Vendor-melted glass 13 varies by up to 4 mole % from the target composition. Specifically, the barium content is too low and the silicon content is too high. Strontium contamination is also significant. This major decrease in the modifier/former ratio between the target and vendor compositions will significantly affect crystallization behavior.

Ambient X-Ray Diffraction

Figure 13 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. Both the Alfred-melted and vendor-melted glass appear to have a significantly higher amorphous content, as evidenced by the amorphous scattering between 25° and 35° 2θ.

Figure 13: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 13, after crystallization at 900°C for 12 hours.

Figure 14 shows a Rietveld refinement of Alfred-melted glass 13. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) low quartz. Other phases cannot be identified. Figure 15 shows a Rietveld refinement of Vendor-melted glass 13. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) low quartz. The diffraction pattern can also be fitted using a triclinic phase. Cell parameters for the three phases are shown in Table 6.

i)

ii)

Figure 14: Rietveld refinement of crystallized Alfred-melted Glass 13, showing presence of i) BaAl₂Si₂O₈ (heavy blue line) and ii) low quartz (green line).

i)

ii)

iii)

Figure 15: Rietveld refinement of crystallized Vendor-melted Glass 13, showing presence of i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ (heavy blue line), ii) low quartz (green line), and iii) triclinic phase (heavy blue line).

Table 6: Unit cell parameters for phases present in crystallized Glass 13.

Phase	S. G.	Lattice Parameters	Cell Angles
BaAl ₂ Si ₂ O ₈	P6/mmm (191)	5.29 x 5.29 x 7.78	90 x 90 x 90
Low Quartz	P3221 (154)	4.82 x 4.82 x 5.61	90 x 90 x 90
Unknown (1)	P1 (1)	6.66 x 4.22 x 6.07	82 x 62 x 77

High-Temperature X-Ray Diffraction

Alfred-melted and vendor-melted glasses were heated at 20°C/min, with measurement intervals of 50°C. Figure 16 shows diffraction patterns from Alfred-melted glass 13. Crystallization is first observed at 850°C. The glass is fully crystallized at 900°C. Figure 17 shows diffraction measurements for vendor-melted glass 13. Crystallization is first observed at 950°C. The glass is fully crystallized after several measurements at 1000°C. These results support those observed from contact angle experiments. These figures show the glasses to crystallize the same phases, however the ratios of these phases are significantly different.

Figure 16: High-temperature X-ray diffraction measurements of Alfred-melted glass 13.

Figure 17: High-temperature X-ray diffraction measurements of Vendor-melted glass 13.

The kinetics of crystallization of vendor-melted glass 13 were observed at 900°C. Figure 18 shows a sequence of HTXRD measurements of vendor-melted glass 13 deposited on a YSZ bilayer. Measurements were made at 900°C, with 170 second intervals. Five major diffraction peaks are observed: 24.3°, 28.6°, 36.9°, 37.7°, 44.6°.

Figure 18: High-temperature X-ray diffraction measurements of vendor-melted glass 13 at 900°C. Measurement intervals were 170 seconds. Measurement was made using Co K_{α} radiation.

Application of JMA theory shows the crystal growth of the 24.3° and 36.9° peaks to follow Avrami-Erofe'ev (A_2) kinetics. This theory holds for continuous crystal networks, where growth is halted by the impingement of crystals upon one another. This is supported by the SEM images for crystallized vendor-melted glass 13. The rate of crystallization of Glass 13 is several orders of magnitude slower than EG9207 at the same temperature. Table 7 summarizes Avrami exponents and rate constants for crystal growth in this glass at 900°C. The similarity in the rate constants for the 24.3 and 36.9 peaks suggest these are characteristic of a single phase.

Table 7: Kinetic parameters for the crystallization of vendor-melted glass 13 at 900°C.

	24.3° 2 θ	36.9° 2 θ
Temperature	900	900
Avrami Exponent	2.0	1.9
A_2 Rate / s ⁻¹	$(2.4 \pm 0.1) \times 10^{-4}$	$(2.6 \pm 0.1) \times 10^{-4}$
EG9207 F_1 Rate / s ⁻¹	$\sim 1 \times 10^{-2}$	

3. SEM Imaging

Alfred-melted and vendor-melted glasses were crystallized according to the method detailed above. Figure 19 shows Alfred-melted glasses in SE mode (left) and BSE mode (right). The images show a continuous crystalline network. BSE images show four distinct levels of contrast, in order of density, a dark rectangular phase (10 μm x 2 μm), a needle-like phase (0.5 μm x 5 μm), an abundant matrix and bright plate-like phase of 1 μm diameter. The dark regions

represent a low-density phase, most likely a silicate or borate, while the brighter phases probably contain barium.

Figure 20 shows vendor-melted glass 13 in SE mode (left) and BSE mode (right). The continuous crystal network is much coarser than that observed in the Alfred-melted glass. Discrete amorphous regions are absent. The BSE images show three distinct regions. The bright region dominates, with smaller regions of lower and higher electron density.

Figure 19: SEM images of Alfred-melted glass 13 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 20: SEM images of vendor-melted glass 13 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

4. Contact Angle Measurements

Glass powders of 2 μm diameter x 5 mm height were melted on alumina substrates, with a heating rate of 5°C/min. Images were collected at 1 minute intervals. Contact angle and sample height were calculated automatically. Figure 21 shows the variation in contact angle and sample

height with temperature. Table 8 shows images of the glasses at critical points during melting. Melting behavior is similar up to 850°C, at which point the Alfred-melted glass maintain shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature.

Figure 21: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 13.

Table 8: Images of Alfred-melted and vendor-melted glass 13 on alumina substrates, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 13	Vendor Glass 13
25°C	25°C
777°C, 90°, 95%	760°C, 70°, 95%
900°C, 108°, 77%	900°C, 114°, 63%
1000°C, 109°, 76%	1000°C, 90°, 50%

Glass 14

Ambient X-Ray Diffraction

Heat treatment at 900°C/12h results in significant crystalline phase formation, as shown in Figure 22. Phase(s) are unidentified.

Figure 22: Ambient X-ray diffraction measurements of Alfred-melted glass 14, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Figure 23: High-temperature X-ray diffraction measurements for SOFC sealing glass 14, between 500°C and 1000°C.

Crystallization of glass 14 is first observed at 850°C, as shown in Figure 23.

No further experiments on glass 14 were conducted.

Glass 15

As illustrated in Figure 1.1, the compositions of the Alfred-melted glass 15 and vendor-melted glass 15 are significantly different. The composition of the vendor-melted glass is high in SiO_2 (3 mole %), low in BaO (3 mole %) and high in SrO (1 mole %).

Ambient X-Ray Diffraction

Figure 24 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. The vendor-melted glass appears to have a significantly higher amorphous content, as evidenced by the amorphous scattering between 25° and 35° 2θ . Crystal phases are unidentified.

Figure 24: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 15, after crystallization at 900°C for 12 hours.

Figure 25 shows a Rietveld refinement of Alfred-melted glass 15. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) high cristobalite. A triclinic phase can be fitted to the data (iii). Figure 26 shows a Rietveld refinement of Vendor-melted glass 15. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) low cristobalite. The diffraction pattern can also be fitted using a triclinic phase (iii). Cell parameters for the three phases are shown in Table 9.

Table 9: Unit cell parameters for phases present in crystallized Glass 15.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	5.30 x 5.30 x 7.80	90 x 90 x 90
High Cristobalite	Fd-3mZ (227)	7.23 x 7.23 x 7.23	90 x 90 x 90
Low Cristobalite	P41212 (92)	5.18 x 5.18 x 6.78	90 x 90 x 90
Unknown (1)	P1 (1)	6.66 x 4.20 x 6.11	80 x 62 x 77

i)

ii)

iii)

Figure 25: Rietveld refinement of crystallized Alfred-melted Glass 15, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, ii) high cristobalite and iii) a triclinic phase.

i)

ii)

iii)

Figure 26: Rietveld refinement of crystallized Vendor-melted Glass 15, showing i) BaAl₂Si₂O₈, ii) low cristobalite and iii) a triclinic phase.

High-Temperature X-Ray Diffraction

Figure 27 shows diffraction patterns from Alfred-melted glass 15. Crystallization is first observed at 850°C. The glass is fully crystallized at 900°C. Figure 28 shows diffraction measurements for vendor-melted glass 15. Crystallization is first observed at 900°C. The glass is fully crystallized at 950°C.

Figure 27: High-temperature X-ray diffraction measurements of Alfred-melted glass 15.

Figure 28: High-temperature X-ray diffraction measurements of Vendor-melted glass 15.

Scanning Electron Microscopy

Figure 29 shows Alfred-melted glass at 1000X in SE (left) and BSE (right) modes. A dense network of crystalline material can be observed, with no obvious amorphous content. BSE images show three distinct levels of contrast. Dark regions are most likely a SiO_2 phase. The brighter phases likely contain barium.

Figure 29 shows Vendor-melted glass in SE mode (left) and BSE mode (right). The images show a continuous crystal network with amorphous regions dispersed throughout the glass. The

BSE images show poor contrast between these regions, indicating that barium level does not vary significantly between the glassy and crystalline regions. Microcracks are present along crystal boundaries.

Figure 29: SEM images of Alfred-melted glass 15 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 30: SEM images of Vendor-melted glass 15 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Hot Stage Microscopy

Figure 31 shows the variation in i) contact angle and ii) sample height with temperature. Table 10 shows images of the glasses at critical points during melting. Melting behavior is similar up to 850°C, at which point the Alfred-melted glass maintain the current shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature. These results support those observed from HTXRD experiments.

Figure 31: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 15.

Table 10: Images of Alfred-melted and vendor-melted glass 15 on alumina substrates, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 15	Vendor Glass 15
25°C	25°C
762°C, 88°, 95%	770°C, 80°, 95%
900°C, 114°, 70%	900°C, 122°, 62%
1000°C, 117°, 70%	1000°C, 85°, 42%

Glass 16

Ambient X-Ray Diffraction

Heat treatment at 900°C/12h results in significant crystalline phase formation, as shown in Figure 32. Phase(s) are unidentified.

Figure 32: Ambient X-ray diffraction measurements of Alfred-melted glass 14, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Crystallization of glass 16 is first observed at 900°C, as shown in Figure 33.

Figure 33: High-temperature X-ray diffraction measurements for SOFC sealing glass 16, between 500°C and 1000°C.

No further experiments on glass 16 were conducted.

Glass 17

Ambient X-Ray Diffraction

Figure 34 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. The vendor-melted glass appears to have a significant amorphous content, as evidenced by the amorphous scattering between 25° and 35° 2θ .

Figure 34: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 17, after crystallization at 900°C for 12 hours.

Figure 35 shows a Rietveld refinement of crystallized Alfred-melted glass 17. The material contains $\text{BaAl}_2\text{Si}_2\text{O}_8$ and an indexed triclinic phase. The results for the vendor-melted glass are shown in Figure 36. Table 11 shows unit cell parameters.

Table 11: Lattice parameters for crystal phases present in crystallized Alfred-melted glass 17.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	$5.29 \times 5.29 \times 7.78$	$90 \times 90 \times 90$
High Cristobalite	Fd-3mZ (227)	$7.14 \times 7.14 \times 7.14$	$90 \times 90 \times 90$
Unknown (1)	P1 (1)	$6.66 \times 4.17 \times 6.07$	$82 \times 62 \times 77$

i)

ii)

Figure 35: Rietveld refinement of Alfred-melted glass 17, crystallized at 900°C for 12 hours. The glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) an unidentified P(1) triclinic phase.

i)

ii)

iii)

Figure 36: Rietveld refinement of Alfred-melted glass 17, crystallized at 900°C for 12 hours. The glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, high cristobalite and ii) an unidentified P(1) triclinic phase.

High Temperature X-Ray Diffraction

Figure 37 shows diffraction patterns from Alfred-melted glass 17, heated at 20°C/min with measurement intervals of 50°C. Crystallization is first observed at 900°C. The glass is fully crystallized at 1000°C. The figure appears to show different components crystallizing at different temperatures. Vendor-melted Glass 17 first shows crystallization at 950°C, as shown in Figure 38. The glass is fully crystallized during the first measurement at 1000°C.

Figure 37: High-temperature X-ray diffraction measurements of Alfred-melted glass 17.

Figure 38: High-temperature X-ray diffraction measurements of Vendor-melted glass 17.

Scanning Electron Microscopy

Figure 39 shows Alfred-melted glasses at 1000X in SE mode (left) and BSE mode (right). The images show a continuous amorphous region with discrete crystalline clusters. The images show at least four levels of contrast, suggesting the presence of three crystalline species. The darkest

needle-like phase is most likely a SiO_2 polymorph (quartz or cristobalite). The crystalline species with similar contrast to the amorphous region is likely a barium silicate species (perhaps $\text{BaAl}_2\text{Si}_2\text{O}_8$), while the brightest phase may be a barium strontium silicate. The amorphous content of this glass appears to be significantly greater than that observed in Alfred-melted glasses 13 and 15.

Vendor-melted glass 17, crystallized at 900°C for 12 hours, is shown at 1000X in Figure 40. The crystalline content of the vendor-melted glass is significantly lower than the Alfred-melted glass, the result of the increased SiO_2 and reduced BaO levels. SiO_2 appears to be abundant, but the content of the other two species is much reduced. The low crystallinity probably renders this glass unsuitable for the SOFC sealing application.

Figure 39: SEM images of Alfred-melted glass 17 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications 1000X.

Figure 40: SEM images of Vendor-melted glass 17 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Hot Stage Microscopy

Figure 41 shows the variation in contact angle and sample height with temperature. Table 12 shows images of the glasses at critical points during melting. Melting behavior of the Alfred-melted and vendor-melted glasses is similar up to around 900°C, at which point the Alfred-melted glass maintain shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature. The melting behavior of the vendor-melted glass was very similar on alumina, coated Ebrite, YSZ bilayer and oxidized anode.

When compared to other Alfred-melted glasses of this series, the contact angle results suggest this glass is suitably fluid at sealing temperature to seal SOFC components at 900°C.

Figure 41: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 17 on various substrates.

Table 12: Images of Alfred-melted and vendor-melted glass 17 on various substrates, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 17 on Alumina	Vendor Glass 17 on Alumina	Vendor Glass 17 on coated Ebrite	Vendor Glass 17 on YSZ bilayer
25°C	25°C	25°C	25°C
772°C, 82°, 95%	783°C, 85°, 95%	778°C, 82°, 95%	779°C, 82°, 95%
900°C, 115°, 70%	900°C, 126°, 73%	900°C, 119°, 69%	900°C, 116°, 71%
1000°C, 115°, 66%	1000°C, 50°, 29%	1000°C, 68°, 37%	1000°C, 56°, 29%

Glass 18

Ambient X-Ray Diffraction

Figure 42 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. Crystal phases are identified by Rietveld refinement as shown in Figure 43 and Figure 44. Glass 18 shows presence of $\text{BaAl}_2\text{Si}_2\text{O}_8$ and an unidentified triclinic phase. Lattice parameters are shown in Table 13.

Figure 42: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 18, after crystallization at 900°C for 12 hours.

Table 13: Unit cell parameters for phases present in crystallized Glass 18.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	5.29 x 5.29 x 7.84	90 x 90 x 90
Low Quartz	P3221 (154)	4.75 x 4.75 x 5.37	90 x 90 x 90
Unknown (1)	P1 (1)	6.52 x 4.22 x 6.16	82 x 64 x 77

i)

ii)

Figure 43: Rietveld refinement of crystallized Alfred-melted Glass 18, showing i) BaAl₂Si₂O₈ and ii) a triclinic phase.

i)

ii)

iii)

Figure 44: Rietveld refinement of crystallized vendor-melted Glass 18, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, ii) low quartz and iii) a triclinic phase.

High-Temperature X-Ray Diffraction

Figure 45 shows diffraction patterns from Alfred-melted glass 18, heated at 20°C/min with measurement intervals of 50°C. Crystallization is first observed at 900°C. The glass is fully crystallized at 950°C. Figure 46 shows measurements for vendor-melted glass 18. Crystallization is first observed at 950°C. The crystal content continues to increase when held at 1000°C.

Figure 45: High temperature X-ray diffraction measurements of Alfred-melted glass 18.

Figure 46: High-temperature X-ray diffraction measurements of Vendor-melted glass 18.

Scanning Electron Microscopy

Figure 47 shows Alfred-melted glasses in SE mode (left) and BSE mode (right). Figure 48 shows vendor-melted glasses in SE mode (left) and BSE mode (right). The images show discrete amorphous regions of 10 μm and two crystalline phases. The needle-like phase is cristobalite. The second crystalline phase appears to contain barium, as evidenced by the bright contrast in the BSE images. The overall crystal content falls between that of Glass 17 (high-amorphous content) and Glasses 13 and 15 (high crystal content).

Figure 47: SEM images of Alfred-melted glass 18 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 48: SEM images of Vendor-melted glass 18 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Hot Stage Microscopy

Figure 49 shows the variation in contact angle and sample height with temperature. Table 14 shows images of the glasses at critical points during melting. Melting behavior of the Alfred-melted and vendor-melted glasses is similar up to around 850°C, at which point the Alfred-melted glass maintain shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature.

Figure 49: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 18 on various substrates.

Table 14: Images of Alfred-melted and vendor-melted glass 18 on alumina, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 18	Vendor Glass 18
25°C	25°C
789°C, 87°, 95%	791°C, 63°, 95%
900°C, 104°, 77%	900°C, 110°, 72%
1000°C, 107°, 75%	1000°C, 62°, 32%

Glass 20

Ambient X-Ray Diffraction

Figure 50 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. Phases are not identified.

Figure 50: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 20, after crystallization at 900°C for 12 hours.

A Rietveld refinement of Alfred-melted Glass 20 shows presence of $\text{BaAl}_2\text{Si}_2\text{O}_8$, low quartz and an unidentified triclinic phase (see Figure 51, Figure 52). Lattice parameters are shown in Table 15.

Table 15: Unit cell parameters for phases present in crystallized Glass 20.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	5.29 x 5.29 x 7.82	90 x 90 x 90
Low Quartz	P3221 (154)	4.83 x 4.83 x 5.38	90 x 90 x 90
Low Cristobalite	P41212 (92)	5.11 x 5.11 x 7.31	90 x 90 x 90
Unknown (1)	P1 (1)	6.52 x 4.15 x 6.16	82 x 64 x 77

i)

ii)

iii)

Figure 51: Rietveld refinement of crystallized Alfred-melted Glass 20, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, ii) low quartz and iii) a triclinic phase.

i)

ii)

iii)

Figure 52: Rietveld refinement of crystallized vendor-melted Glass 20, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, ii) low cristobalite and iii) a triclinic phase.

High-Temperature X-Ray Diffraction

Figure 53 shows diffraction patterns from Alfred-melted glass 20, heated at 20°C/min with measurement intervals of 50°C. Crystallization is first observed at 850°C. The intensity of the 31° 2 θ peak increases between 850°C and 1000°C. Vendor-melted glass 20 begins crystallizing at 850°C, and is fully crystallized at 950°C, as shown in Figure 54.

Figure 53: High-temperature X-ray diffraction measurements of Alfred-melted glass 20.

Figure 54: High-temperature X-ray diffraction measurements of Vendor-melted glass 20.

Scanning Electron Microscopy

Figure 55 shows vendor-melted glasses in SE mode (left) and BSE mode (right). Figure 56 shows vendor-melted glasses in SE mode (left) and BSE mode (right). The SE images a dense network of crystalline phases, similar to that observed in glasses 13, 15 and 23. The BSE images show three distinct levels of contrast, suggesting the presence of three distinct phases.

Figure 55: SEM images of Alfred-melted glass 20 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 56: SEM images of vendor-melted glass 20 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Hot Stage Microscopy

Figure 57 shows the variation in contact angle and sample height with temperature. Table 16 shows images of the glasses at critical points during melting. Melting behavior of the Alfred-melted and vendor-melted glasses is similar up to around 850°C, at which point the Alfred-melted

glass maintain shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature. The melting behavior of the vendor-melted glass was very similar on alumina, coated Ebrite, YSZ bilayer and oxidized anode.

Figure 57: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 20 on alumina.

Table 16: Images of Alfred-melted and vendor-melted glass 17 on alumina, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 20	Vendor Glass 20
25°C	25°C
768°C, 89°, 95%	763°C, 82°, 95%
900°C, 86°, 77%	900°C, 101°, 66%
1000°C, 86°, 70%	1000°C, 101°, 57%

Glass 21

Ambient X-Ray Diffraction

Heat treatment at 900°C/12h results in significant crystalline phase formation, as shown in Figure 58. Phase(s) are unidentified.

Figure 58: Ambient X-ray diffraction measurements of Alfred-melted glass 21, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Crystallization of glass 21 is first observed at 800°C, as shown in Figure 59.

Figure 59: High-temperature X-ray diffraction measurements for SOFC sealing glass 21, between 500°C and 1000°C.

No further experiments on glass 21 were conducted.

Glass 23

Ambient X-ray Diffraction

Figure 60 shows a significant difference between the diffraction patterns of Alfred-melted and vendor-melted glasses. The vendor-melted glass appears to have a greater amorphous content than the Alfred-melted glass, as evidenced by the amorphous scattering between 25° and 35° 2θ . Crystal phases are unidentified.

A Rietveld refinement of Alfred-melted Glass 23 shows presence of $\text{BaAl}_2\text{Si}_2\text{O}_8$, cristobalite and an unidentified triclinic phase, Figure 61. Lattice parameters are shown in Table 17. Phase identification for the vendor-melted glass is shown in Figure 62.

Figure 60: Ambient X-ray diffraction measurements of Alfred-melted and vendor-melted glass 23, after crystallization at 900°C for 12 hours.

Table 17: Unit cell parameters for phases present in crystallized Glass 23.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	5.29 x 5.29 x 7.84	90 x 90 x 90
Low Cristobalite	P41212 (92)	5.09 x 5.09 x 6.93	90 x 90 x 90
High Cristobalite	Fd3mZ (227)	7.26 x 7.26 x 7.26	90 x 90 x 90
Unknown (1)	P1 (1)	6.49 x 4.13 x 6.18	82 x 64 x 77

i)

ii)

iii)

Figure 61: Rietveld refinement of crystallized Alfred-melted Glass 23, showing i) BaAl₂Si₂O₈, ii) low cristobalite and iii) a triclinic phase.

i)

ii)

iii)

Figure 62: Rietveld refinement of crystallized vendor-melted Glass 23, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$, ii) high cristobalite and iii) a triclinic phase.

High Temperature X-Ray Diffraction

Figure 63 shows diffraction patterns from Alfred-melted glass 23. Crystallization is first observed at 900°C, above which temperature the crystal content does not change significantly. Figure 64 shows diffraction patterns from vendor-melted Glass 23. Crystallization is first observed at 900°C. The glass is fully crystallized at 950°C.

Figure 63: High-temperature X-ray diffraction measurements of Alfred-melted glass 23.

Figure 64: High-temperature X-ray diffraction measurements of vendor-melted glass 23.

Scanning Electron Microscopy

Figure 65 shows Alfred-melted glasses in SE mode (left) and BSE mode (right). Figure 66 shows vendor-melted glasses in SE mode (left) and BSE mode (right). The images show a continuous crystal network with no visible amorphous regions. The BSE images show poor contrast between these regions, indicating that barium level does not vary significantly between the glassy and crystalline regions.

Figure 65: SEM images of Alfred-melted glass 23 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 66: SEM images of Vendor-melted glass 23 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Hot Stage Microscopy

Figure 67 shows the variation in contact angle and sample height with temperature. Table 18 shows images of the glasses at critical points during melting. Melting behavior is similar up to 850°C, at which point the Alfred-melted glass maintain shape, while the vendor-melted glass deforms. This is indicative of the onset of crystallization in the Alfred-melted glass at this temperature. The vendor-melted glass appears to crystallize at a higher temperature.

Figure 67: Variation in contact angle (upper) and sample height (lower) with temperature of Alfred-melted and vendor-melted glass 23.

Table 18: Images of Alfred-melted and vendor-melted glass 23 on alumina substrates, at sintering temperature (95% sample height), 900°C and 1000°C.

Alfred Glass 23	Vendor Glass 23
<p>25°C</p>	<p>25°C</p>
<p>786°C, 85°, 95%</p>	<p>780°C, 92°, 95%</p>
<p>900°C, 84°, 78%</p>	<p>900°C, 109°, 72%</p>
<p>1000°C, 87°, 78%</p>	<p>1000°C, 96°, 54%</p>

Glass 24

Ambient X-Ray Diffraction

Heat treatment at 900°C/12h results in significant crystalline phase formation, as shown in Figure 68. Phase(s) are unidentified.

Figure 68: Ambient X-ray diffraction measurements of Alfred-melted glass 24, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Crystallization of glass 24 is first observed at 800°C, as shown in Figure 69.

Figure 69: High-temperature X-ray diffraction measurements for SOFC sealing glass 24, between 500°C and 1000°C.

No further experiments on glass 24 were conducted.

Glass 26

Ambient X-Ray Diffraction

Figure 70 shows a significant difference between the diffraction patterns glass 26 after two different heat treatments. Both samples contain $\text{BaAl}_2\text{Si}_2\text{O}_8$. At least two other unidentified phases are present. Figure 71 shows PDF cards that match the data reasonably well. The major diffraction peak however does not match any of these phases.

Figure 70: Ambient X-ray diffraction measurements of Alfred-melted glass 26, after firing for 12 hours at i) 900°C and ii) 1000°C.

Figure 71: Ambient X-ray diffraction measurements of Alfred-melted glass 26, after firing for 12 hours at 900°C.

Figure 72 shows a Rietveld refinement of Alfred-melted glass 26 after crystallization at 900°C for 12 hours. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and a triclinic phase. Figure 73 shows a Rietveld refinement of Alfred-melted Glass 26 after crystallization at 1000°C for 12 hours. The crystallized glass contains i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) low cristobalite. The diffraction pattern can also be fitted using a triclinic phase (iii). Cell parameters for the three phases are shown in Table 19.

Table 19: Unit cell parameters for phases present in crystallized Glass 26.

Phase	S. G.	Lattice Parameters	Cell Angles
$\text{BaAl}_2\text{Si}_2\text{O}_8$	P6/mmm (191)	5.28 x 5.28 x 7.83	90 x 90 x 90
Unknown (1)	P1 (1)	6.46 x 4.20 x 6.18	80 x 64 x 77

i)

ii)

Figure 72: Rietveld refinement of crystallized Alfred-melted Glass 26, after crystallization at 900°C for 12 hours, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) an unidentified triclinic phase.

i)

ii)

Figure 73: Rietveld refinement of crystallized Alfred-melted Glass 26, after crystallization at 1000°C for 12 hours, showing i) $\text{BaAl}_2\text{Si}_2\text{O}_8$ and ii) an unidentified triclinic phase.

High Temperature X-ray Diffraction

HTXRD analysis of Glass 26 shows formation of up to four phases, as shown in Figure 74. Crystallization of phase D is first observed at 900°C. Phase A crystallizes between 950°C and 1000°C. The peak intensity of phase A does not change after holding at 1000°C for 30 minutes. Phase B crystallizes between 950°C and 1000°C, and increases in intensity during the 1000°C hold. Phase C reaches maximum intensity during the first 1000°C measurement, but decreases in intensity in subsequent measurements. A Rietveld analysis of this data shows the labeled phases do not match $\text{BaAl}_2\text{Si}_2\text{O}_8$, quartz or cristobalite.

Figure 74: High-temperature X-ray diffraction measurements of Alfred-melted glass 26.

Scanning Electron Microscopy

Analysis of crystallized Glass 26 by SEM reveals two distinct temperature-dependent microstructures. Crystallization at 900°C (Figure 75), shows formation of indistinct crystal clusters, with formation of a needle-like phase in an amorphous matrix. Crystallization at 1000°C results (Figure 76) in extensive formation of the needle-like phase, without the dense clusters observed in the 900°C sample.

Figure 75: SEM images of Alfred-melted glass 26 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 76: SEM images of Alfred-melted glass 26 in SE mode (left) and BSE mode (right), after crystallization at 1000°C for 12 hours. Images show magnifications of 1000X.

Glass 33

Ambient X-Ray Diffraction

Figure 77 shows the ambient diffraction measurement for Glass 33. The glass is significantly crystalline, but phase(s) are unidentified.

Figure 77: Ambient X-ray diffraction measurements of Alfred-melted Glass 33, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Figure 78 shows the XRD sequence for Glass 33, heated at 2°C/min on an alumina substrate. Crystallization is first observed at 850°C. Peaks labeled 'A' crystallize at 900°C and reach a stable intensity from 950°C and above. These peaks appear to be characteristic of the same phase. Peaks labeled 'B' crystallize at 850°C and reach a stable intensity from 900°C and above. These peaks appear to be characteristic of a different phase to Phase 'A'. If the glass was held at 900°C during sealing, the intensity of peaks 'A' would be expected to increase until the maximum intensity was reached. A third phase (peak at 33° 2 θ) appears at 850°C but is not present at 900°C or higher.

Figure 78: HTXRD sequence for Glass 33, heated at 2°C/min.

Scanning Electron Microscopy

Alfred-melted Glass 33, when crystallized according to the method detailed previously, exhibited a white outer layer of less than 1mm in thickness, while the interior of the pellet was gray. The interior and surface had a similar crystalline microstructure. This behavior was observed in pellets fired in different furnaces, and is therefore not due to furnace contamination.

Figure 79 shows the surface of the crystallized Glass 33 sample in SE mode (left) and BSE mode (right). Figure 80 shows the interior of the pellet in SE mode (left) and BSE mode (right). The images show a dense continuous crystalline network.

Figure 79: SEM images of the surface of Alfred-melted glass 33 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Figure 80: SEM images of the interior of Alfred-melted glass 33 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Glass 35

Ambient X-Ray Diffraction

Figure 81 shows the diffraction measurement for Glass 35. The glass is significantly crystalline, but phase(s) are unidentified.

Figure 81: Ambient X-ray diffraction measurements of Alfred-melted Glass 35, after crystallization at 900°C for 12 hours.

High-Temperature X-Ray Diffraction

Figure 82 shows the XRD sequence for Glass 35, heated at 2°C/min on an alumina substrate. Crystallization is first observed at 800°C. Peak 'A' crystallizes slowly between 800°C and 900°C. From 900°C to 1000°C, the intensity of this peak is constant. Peak 'B' crystallizes between 800°C and 850°C. From 850°C to 1000°C the intensity of this peak is constant. The peak at 28°2θ (C) appears to belong to a third phase, however more experiments are being completed to investigate this further. It appears this phase decreases in concentration between 950°C and 1000°C. The diffraction pattern changes very little between 900°C and 950°C. The most significant change is that of the 26°2θ peak (D), which changes from a doublet to a single peak of greater intensity. This can be fully attributed to thermal expansion differences between the phases contributing to this peak. If held at 900°C, the diffraction pattern would not be expected to change.

Figure 82: HTXRD sequence for Glass 35, heated at 2°C/min.

Scanning Electron Microscopy

Figure 83 shows the surface of the crystallized Glass 35 sample in SE mode (left) and BSE mode (right). Figure 83 shows the interior of the pellet in SE mode (left) and BSE mode (right). The images show a dense continuous crystalline network.

Figure 83: SEM images of the surface of Alfred-melted Glass 35 in SE mode (left) and BSE mode (right), after crystallization at 900°C for 12 hours. Images show magnifications of 1000X.

Glass G18

Figure 84 shows the diffraction measurement for Glass G18. The glass is significantly crystalline, but phase(s) are unidentified.

Figure 84: Ambient X-ray diffraction measurements of Alfred-melted Glass G18, after crystallization at 800°C for 12 hours.

High Temperature X-Ray Diffraction

Figure 85 shows the XRD sequence for Glass G18, heated at 2°C/min on a YSZ substrate. The intensity of the crystalline peaks decreases as the temperature reaches 900°C and the peaks disappear at 1000°C, which implies the melting of the crystalline phase. This is supported by the data of the contact measurement of G18, in which the contact angle decreases abruptly at temperature near 1000°C.

Figure 85: HTXRD sequence for Glass G18, heated at 2°C/min.

Scanning Electron Microscopy

Alfred-melted Glass G18 was crystallized according to the method detailed above. Figure 86 shows the surface of the crystallized Glass G18 sample in SE mode (left) and BSE mode (right). The images show a dense continuous network of a needle-like phase.

Figure 86: SEM images of the surface of Alfred-melted Glass G18 in SE mode (left) and BSE mode (right), after crystallization at 750°C for 12 hours. Images show magnifications of 1000X.

Experiment Summary

For reference, the full experimental matrix, with experiment numbers, are shown in Table 20.

Table 20: Compilation of experiments performed to date on the SOFC sealants.

Experiment Number	Glass	Alfred or Vendor	Experiment Type
0541	13	A	HTXRD 900°C
0541b	13	A	Ambient 900°C/12h
0541c	13	A	HTXRD 1000°C
0555	13	A	HTXRD Kinetics 800°C, 230s
0556	13	A	HTXRD Kinetics 850°C, 230s
0557	13	A	HTXRD Kinetics 900°C, 230s
0565	13	A	Ambient 800°C/5h
0565b	13	A	Ambient 825°C/5h
0565c	13	A	Ambient 810°C/5h
0636	13	A	HTXRD 1000°C
0612	13	V	Ambient 900°C/12h
0622	13	V	HTXRD 1000°C
0624	13	V	HTXRD Kinetics 900°C, 230s
0625	13	V	HTXRD Kinetics 950°C, 230s
0591	14	A	HTXRD 1000°C
0593	14	A	Ambient 900°C/12h
0595	15	A	HTXRD 1000°C
0596	15	A	Ambient 900°C/12h
0637	15	A	HTXRD 1000°C
0613	15	V	Ambient 900°C/12h
0623	15	V	HTXRD 1000°C
0627	15	V	HTXRD Kinetics 900°C, 230s
0592	16	A	HTXRD 1000°C
0594	16	A	Ambient 900°C/12h
0599	17	A	HTXRD 1000°C
0601	17	A	Ambient 900°C/12h
0611	17	V	Ambient 900°C/12h
0628	17	V	HTXRD 1000°C
0600	18	A	HTXRD 1000°C
0602	18	A	Ambient 900°C/12h
0614	18	V	Ambient 900°C/12h
0629	18	V	HTXRD 1000°C
0584	19	A	Ambient 900°C/12h
0586	19	A	HTXRD 900°C
0586b	19	A	HTXRD 1000°C
0583	20	A	Ambient 900°C/12h
0585	20	A	HTXRD 900°C

0585c	20	A	HTXRD 1000°C
0615	20	V	Ambient 900°C/12h
0634	20	V	HTXRD 1000°C
0588	21	A	HTXRD 1000°C
0589	21	A	Ambient 900°C/12h
0597	23	A	HTXRD 1000°C
0598	23	A	Ambient 900°C/12h
0616	23	V	Ambient 900°C/12h
0635	23	V	HTXRD 1000°C
0580	24	A	HTXRD 900°C
0580b	24	A	HTXRD 1000°C
0582	24	A	Ambient 900°C/12h
0587	24	A	Ambient 900°C/12h
0630	26	A	HTXRD 1000°C
0632	26	A	Ambient 900°C/12h
0670	33	A	Ambient 900°C/12h
0671	33	A	HTXRD 1000°C
0685	33	A	HTXRD 1000°C
0687	35	A	HTXRD 1000°C
0687b	35	A	Ambient 900°C/12h
0686	G18	A	HTXRD 1000°C
0686b	G18	A	Ambient 800°C/12h

Ambient Experiments: Powdered glass pressed into 0.7" pellet at 10,000 pounds for 60 seconds. Pellets fired on alumina substrates to 900°C for 12 hours.

HTXRD Experiments: Powdered glass deposited on specified substrate, heated at specified heating rate to indicated temperature, with measurements at 50°C intervals.

HTXRD Kinetics Experiments: As above, heated at 200°C/min to specified temperature. Isothermal measurements made at indicated time interval.

4.5. Use of fillers in the sealing glasses

Extensive measurements were performed to evaluate the wetting behavior of sealing glasses in contact with the SOFC components. The study addresses not only the fundamental science of wetting and reactivity but also has implications in predicting the gap filling behavior of the sealants.

Two distinct experiment sets were performed that included the sealing glass in its pure form and then the sealant glass with added fillers that are potentially important for gap filling to meet the hermeticity requirements. A total of 48 material combinations were tested with variations as follows:

- Four substrate conditions, including: the zirconia side of the fuel cell bilayer, the as-manufactured metal interconnect surface, the preoxidized metal interconnect surface, and finally one modified metal surface.
- Two different filler materials with two particle size distributions each
- Four different filler loadings.

An example of the effects of YSZ filler on the base glass sealant, EG9207, is shown in Figure 87. In general, increasing the loading of inert fillers resulted in less sample sintering as demonstrated by the sample height vs. temperature behavior. The results of the contact angle measurements, which contain a larger error, do not show marked differences as a result of filler loading. Therefore, although the filler is expected to decrease the flow of the sealant, it is also expected to improve sealant's gap filling behavior.

Figure 87: Effect of YSZ filler on the behavior of the base glass, EG9207, when in contact with the YSZ electrolyte. Volume fraction loadings are indicated in the figures.

4.6. Effect of Glass Particle Size on Crystallization Kinetics

The effects of the particle size distribution (PSD) in the SOFC frit powders on wetting behavior and seal densification, as well as the crystallization rate, was studied in some detail. Increasing

the PSD increases the sintering temperature (defined by a 5% reduction in initial sample height) from 641°C for the 10 μm frit (average of two measurements) to 650°C (average) for the 23 μm frit. This can be attributed to a reduction in particle-particle contact, due to the reduced packing density of the coarser frit. Results are shown in Figure 88.

Secondly, the maximum contact angle decreases from 140° at 766°C to 124° at 772°C. As shown in Figure 89, the contact angle and sample height at 925°C appear to be unchanged by the change in frit size. The higher contact angle data, in the case of the 10 μm frit, can be attributed to entrapped bubbles in the glass causing an increase in viscosity. The increase in viscosity acts to reduce the effect of surface tension, thus hindering sphere formation.

Figure 88: Variation in sample height of EG9207 with varying frit particle size on YSZ and untreated Ebrite.

Figure 89: Variation in contact angle of EG9207 with varying frit particle size on YSZ and untreated Ebrite. Duplicate measurements are shown.

The effect on crystallization kinetics and contact angle of the particle size distribution (PSD) of the SOFC sealing glass has been investigated. Again, if we anticipate that surface nucleation occurs, it is likely that the particle size of the initial glass will have some effect on the rate of crystallization. To explore this theory, glasses with two particle size distributions were studied using HTXRD. Isothermal kinetics analysis was performed at 5 or 7 different temperatures for the base glass EG9207 with two different particle size distributions. By tracking the growth of the XRD peaks for crystalline phases, it is possible to apply the JMA analysis (described in section 4.3.2.b) to determine the crystallization rate and apparent activation energy.

Increasing the PSD from ($d_{50} = 10 \mu\text{m}$) to ($d_{50} = 23 \mu\text{m}$) slowed the crystallization of the glass, as shown in Figure 90. This can be attributed to the change in the number of nucleation sites, which is directly related to the surface area of the frit. Figure 91 shows SEM images of “fully crystallized” glass, melted from the two powder samples. Note that in this case we use “fully crystallized” to define the equilibrium crystalline content of approximately 30 volume percent. The ($d_{50} = 23 \mu\text{m}$) glass has around half the number of crystals as the ($d_{50} = 10 \mu\text{m}$) sample, however the crystal size is much larger.

Figure 90: Arrhenius plot of crystallization of EG9207 with ($d_{50} = 10 \mu m$) and ($d_{50} = 23 \mu m$) frit size distributions.

Figure 91: 500x BSE images of EG9207, melted from ($d_{50} = 10 \mu m$) (left) and ($d_{50} = 23 \mu m$) (right) frit powder.

4.7. Coefficient of thermal expansion for bulk SOFC glasses & glass-ceramics

The CTE of the bulk glasses were found to be 10-12 ppm/K (see Figure 92). The glass transition temperatures (T_g) of the bulk glasses were found to be between 570-700°C. Most components were found to increase the CTE of the bulk glasses in the investigated composition range, if exchanged for silica, especially BaO. ZrO_2 additions decreased the CTE.

Figure 92: $\Delta L/L_0$ expansion curves of investigated glasses.

Because the sealing glasses partially crystallize during the sealing process, it is important to determine the CTE for the glass-ceramics at temperatures below the transformation range. To this end, a series of glasses were prepared as bars from the glass frit powder, then subjected to the target sealing profile. The target sealing profile involves heating to 900°C for 30 minutes, followed by cooling. The CTE results for the glass ceramics are shown in Figure 93. The average expansion from 200°C to 500°C ranges from 10.5 ppm/K (#17b) to 13.3 ppm/K (#35), while the bulk expansion for YSZ is 8.8 ppm/K to 10.3 ppm/K. The TEC for the metal interconnect is 12.1 ppm/K, 20-800°C. Therefore, the CTE matching is an excellent compromise between that of the YSZ and the interconnect.

Figure 93: $\Delta L/L_0$ expansion curves of investigated glass ceramics (insert shows glass numbers).

4.8. Test SOFC, Cell Level – Functional Seal Properties

The functional seal properties were tested by two means, first, by preparing the test vehicles using the new sealing glasses, followed by room temperature leak testing and X-ray radiography. The radiography images provide a visual insight into wetting and void formation, thus providing an important overview of the seal on a macroscopic length scale.

Based on initial hot stage microscopy data and functional seal testing of down-selected glasses, it was apparent that improvements to the wetting characteristics were required. Several approaches were investigated towards improving the wetting characteristics including compositional modifications (i.e. higher $\text{SiO}_2/\text{B}_2\text{O}_3$ ratio) higher sealing temperatures, and higher loads during sealing. Compositional modifications, thus far, have not resulted in improved wetting (see for example Figure 94). Further work in this area is now focused on the use of sintering aids. Sealing temperatures were increased from 900°C to 930°C but only showed marginal improvement in wetting. Increasing the sealing temperature further would adversely affect the interconnect properties. Experiments conducted at GE Research, where load during sealing was increased from 0.1psi to 1psi, showed significant improvement in the wetting characteristics (see Figure 95).

(a)

(b)

Figure 94: (a) X-ray radiography image showing Alfred glass #33 “as-sealed” at 900°C and (b) baseline seal glass “as-sealed” at 900°C.

Figure 95: Radiography images showing (a) Alfred glass #33 sealed at 900°C, 30 min using 1psi load and (b) Alfred glass #33 sealed at 900°C, 30 min using 0.1psi load during sealing.

Figure 96: BSE images showing as-sealed microstructures for glass-ceramics #17, #26, #33, and G-18.

4.9. Environmental Degradation Testing

Downselection based on results shown in previous sections led to a focus on glasses:

1. Base glass composition (EG9207)
2. Alfred 17
3. Alfred 26
4. Alfred 33
5. PNNL G18

Again, it is important to compare the sealing glasses developed in this study to the published G18 composition from PNNL.

Post sealing microstructures for the various Alfred melted glasses are shown in Figure 96. Some key parameters of interest as the data from heat-treated samples is obtained and analyzed include: (1) glass-crystal ratio, (2) glass chemistry, (3) crystalline phases, void formation, and compatibility with cell and interconnect materials. As can be seen from the images in Figure 8.2.2., #17 and #26 appear to be mostly glass with clusters of sub-micron crystallites. Glass ceramic #33 and G18 appeared more crystalline than #17 or #26. In all cases, the sub-micron crystallites are too small for SEM/EDS analysis. Electron microprobe will be used in an attempt to semi-quantify the composition of the crystalline phases. EDS analyses of the glass matrix regions for all the samples showed the presence of components consistent with that of the starting glass composition. Analyses of the microstructures of the heat-treated samples are still being performed.

Heat treatments for degradation tests in static air and wet H₂ have been completed out to 800 hours for Alfred glass #17 and #26, while Alfred glass #33 and G-18 have seen 600 hours. It

should be noted that these tests were conducted without electrical potential. Electrochemical related degradation is being investigated in separate experiments. All samples have been submitted for SEM analysis including *as-sealed* samples. Prior to microstructure analysis, samples were characterized by radiography and leak tested. It is clear from the SEM images that all of the Alfred glasses, which were sealed at 900°C for 30 minutes in air with 0.1psi load, showed non-optimum wetting characteristics (see Figure 97). However, all samples passed the leakage test indicating some degree of sealing was obtained. As mentioned in earlier, improvements in wetting can be obtained by increasing the load during sealing.

Figure 97: Representative SEM images (BSE) showing non-optimum wetting for Alfred glasses

Some key parameters of interest as the data from heat-treated samples is obtained and analyzed include: (1) glass-crystal ratio, (2) glass chemistry, (3) crystalline phases, (4) wetting and void formation, and (5) compatibility with cell and interconnect materials. Post sealing microstructures for the various Alfred melted glasses are shown in Figure 96. As can be seen from the images in Figure 96, #17 and #26 appear to be mostly glass with clusters of sub-micron crystallites. Glass ceramic #33 and G18 appeared more crystalline than #17 or #26. In all cases, the sub-micron crystallites are too small for SEM/EDS analysis. Electron microprobe will be used in an attempt to semi-quantify the composition of the crystalline phases. EDS analyses of the glass matrix regions for all the samples showed the presence of components consistent with that of the starting glass composition. It is also clear from the SEM images (see Figure 97) that all of the Alfred glasses, which were sealed at 900°C for 30 minutes in air with 0.1psi load, showed non-optimum wetting characteristics. However, all samples passed the leakage test indicating some degree of sealing was obtained. As mentioned earlier, improvements in wetting can be obtained by increasing the load during sealing.

Analyses of the microstructures of the heat-treated samples are still being performed. Comparisons to the base line seal glass (EG9207) will be made in order to assess whether the new glass compositions showed an improvement in chemical stability.

4.10. Bulk CTE of lighting sealants

The thermal expansion behavior of the YAS samples has been verified through repeated measurements: The coefficients of thermal expansion (CTE) decrease during dilatometer runs to 1450°C, compared to the initial CTE values measured up to 1000°C. No CTE changes were observed during up to five dilatometer runs to 1000°C, i.e. phase changes are expected between 1000°C and 1450°C, as shown in Figure 98. Table 21 includes the average TEC values for the specimens.

In addition, repeated measurements showed that the CTE changes occurred during the first run to 1450°C, and that the CTE stays constant in further repeated runs to 1450°C. This indicates that the phase transformation kinetics between 1000°C and 1450°C are rapid (the heating and cooling rates during CTE measurements were 4 K/min). XRD and SEM data of samples from before dilatometry showed no presence of a silicate phase, but a glassy phase instead. Samples observed after dilatometry up to 1450°C though, show the presence of the $Y_2Si_2O_7$ beta phase. The phase transformation from the glassy phase to the beta silicate phase apparently decreases the CTE of the system and remains stable at temperatures below 1450°C. Additional HTXRD work can be done to further understand the kinetics of the YAS system and confirm this phase transformation observed in the dilatometer.

Figure 98: $\Delta L/L_0$ expansion curves of investigated YAS ceramics after stabilization through repeated runs to 1000°C and 1450°C (insert shows sample numbers).

Table 21: Coefficients of thermal expansion (CTE) in ppm/K after stabilization through repeated dilatometer runs to 1000°C and 1450°C

#	Stabilization through runs to 1000°C	Stabilization through runs to 1450°C	
		CTE, 100-1000°C	CTE, 100-1450°C
YAS 1	8.79	8.43	9.09
YAS 2	8.70	8.09	8.74
YAS 3	8.40	7.14	7.88

4.11. Electrochemical Degradation Testing

A direct current (DC) conductivity test is currently being implemented at GE Research to study the effect of electric potential on seal glass stability. The seal used in fuel cells needs to be electrically insulating and stable under stack voltage potentials (i.e., no ionic conduction of seal components) to avoid (1) an electrical short in the stack and (2) degradation of the seal. The

baseline seal glass (EG9207) will be evaluated along with the Alfred #33 and the PNNL G18 glasses.

4.12. Phase equilibria studies in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system

A detailed description of the phase equilibria work performed to date, along with structure solutions and TEC measurements for the new phases discovered over the course of the work is provided below.

4.12.1. Quantitative Results of YAS-Series Annealing Studies

Table 1 lists compositions of YAS-series glasses. As-melted samples were provided by GE Global Research. Annealed samples were prepared at GE and Alfred. Figure 99 and Figure 100 show the typical microstructures for the as-melted and annealed samples, respectively, which contain varying amounts of amorphous phase. Extensive XRD, SEM and electron backscattered diffraction was used in the phase identification and structure solution. The series of experiments, with quantitative results, is summarized in Table 22.

Figure 99: 1000X BSE image of YAS-3 as melted. The image shows $\text{Y}_3\text{Al}_5\text{O}_{12}$ (bright phase), Al_2O_3 (dark phase) and an amorphous region (intermediate phase).

Figure 100: 1000X BSE image of YAS-3 after annealing at 1100°C for 10 hours. The image shows $\text{Y}_3\text{Al}_5\text{O}_{12}$ (bright regions), Al_2O_3 (dark regions) and an yttrium silicate growing within an amorphous matrix (intermediate regions).

Table 22: Weight fractions of crystalline phases in YAS-series glasses and Y-Si-O compounds, calculated using the Rietveld method. Any amorphous content is ignored in the calculations.

Sample	Expt	Treatment	% $\text{Y}_3\text{Al}_5\text{O}_{12}$	% Al_2O_3	% $\text{Al}_6\text{Si}_2\text{O}_{13}$	% $\text{Y}_2\text{Si}_2\text{O}_7$	% $\text{Y}_{4.67}\text{Si}_3\text{O}_{13}$	% Y_2SiO_5
YA	0544	As melted	84	16	-	-	-	-
YAS-1	0545	As melted	58	42	-	-	-	-
YAS-1	0607	1200°C/100h	54	25	6	10(α) + 5(β)	-	-
YAS-1	0663	1300°C/100h	53	40	-	7(β)	-	-
YAS-1	0549	1400°C/100h	52	42	-	6(β)	-	-
YAS-1	0649	1400°C/200h	55	40	-	5(β)	-	-
YAS-1	0692	1500°C/100h	61	39	-	-	-	-
YAS-1	0577	1600°C/100h	62	38	-	-	-	-
YAS-1	0666	1600°C/100h	61	39	-	-	-	-
YAS-2	0546	As melted	78	22	-	-	-	-
YAS-2	0608	1200°C/100h	71	23	-	6(β)	-	-
YAS-2	0664	1300°C/100h	62	22	3	13(β)	-	-
YAS-2	0550	1400°C/100h	67	20	-	13(γ)	-	-
YAS-2	0693	1500°C/100h	79	21	-	-	-	-
YAS-2	0578	1600°C/100h	84	16	-	-	-	-
YAS-2	0667	1600°C/100h	79	21	-	-	-	-
YAS-3	0548	As melted	76	24	-	-	-	-
YAS-3	0639	1100°C/10h	58	19	7	16(α)	-	-
YAS-3	0640	1100°C/50h	49	23	8	19(α)	-	-
YAS-3	0641	1100°C/100h	55	20	8	17(α)	-	-
YAS-3	0657	1100°C/150h	56	19	8	17(α)	-	-
YAS-3	0643	1100°C/200h	53	19	9	10(α)+9(β)	-	-
YAS-3	0654	1200°C/10h	58	20	5	18(α)	-	-
YAS-3	0609	1200°C/100h	53	42	-	5(β)	-	-
YAS-3	0658	1200°C/100h	53	21	8	12(α) + 7(β)	-	-
YAS-3	0665	1300°C/100h	51	19	10	20(β)	-	-
YAS-3	0653	1400°C/10h	47	20	12	21(γ)	-	-
YAS-3	0677	1400°C/10h	39	23	11	10(β) + 17(γ)	-	-
YAS-3	0648	1400°C/25h	49	24	7	20(γ)	-	-
YAS-3	0551	1400°C/100h	50	27	-	23(γ)	-	-
YAS-3	0694	1500°C/100h	76	24	-	-	-	-

YAS-3	0579	1600°C/100h	80	20	-	-	-	-
YAS-3	0668	1600°C/100h	77	23	-	-	-	-
YAS-4 ²	0650	As melted	34	-	-	-	66	-
YAS-4 ²	0656	1200°C/100h	37	-	5	-	58	-
YAS-4	0672	1350°C/100h	35	-	-	10(β) + 14(γ)	-	41
YAS-5 ²	0651	As melted						
YAS-5 ²	0655	1100°C/25h						
YAS-5 ¹	0661	1200°C/100h	5	-	32	17(α)+46(β)	-	-
YAS-5	0673	1350°C/100h	6	29	26	39(γ)	-	-
YAS-6 ²	0652	As melted						
YAS-6 ²	0662	1200°C/100h						
YAS-6	0674	1350°C/100h	-	41	3	56(γ)	-	-

² - Weight fractions calculated while at least one minor phase is unidentified

α - $\text{Y}_2\text{Si}_2\text{O}_7$ (P-1)

β - $\text{Y}_2\text{Si}_2\text{O}_7$ (C12/m1)

γ - $\text{Y}_2\text{Si}_2\text{O}_7$ (P1121/b)

δ - $\text{Y}_2\text{Si}_2\text{O}_7$ (Pnam)

I - Y_2SiO_5 (I12/a1)

4.12.2. Quantitative Results of Y_2O_3 - Al_2O_3 - SiO_2 Synthesis Studies

Synthesis of $\text{Y}_2\text{Si}_2\text{O}_7$, Y_2SiO_5 and $\text{Y}_{4.66}\text{Si}_3\text{O}_{13}$ from mixed oxides has been attempted. Results are summarized in Table 23.

$\text{Y}_2\text{Si}_2\text{O}_7$ (γ) and (δ) has been synthesized in phase-pure form using solid-state synthesis of mixed oxides SiO_2 and Y_2O_3 . A small amount of $\text{Y}_2\text{Si}_2\text{O}_7$ (β) was formed at 1300°C. $\text{Y}_2\text{Si}_2\text{O}_7$ (γ) was converted to (δ) by annealing at 1600°C. $\text{Y}_2\text{Si}_2\text{O}_7$ (δ) was converted to (γ) by annealing at 1500°C. Attempts to anneal $\text{Y}_2\text{Si}_2\text{O}_7$ (γ) to (α) or (β) at 1300°C and 1200°C respectively were unsuccessful. This supports the phase relationship published by Ito and Johnson [3]:

Attempts to synthesize yttrium apatite ($\text{Y}_{4.66}\text{Si}_3\text{O}_{13}$) from mixed oxides were unsuccessful. Annealing for 36 hours formed Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$. Additions of alumina were made in an attempt to stabilize the structure. These additions resulted in formation of $\text{Y}_3\text{Al}_3\text{O}_{12}$ in addition to Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$. Y-Apatite formed in as-melted YAS-4, but decomposed to Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$ after annealing. This suggests that $\text{Y}_{4.66}\text{Si}_3\text{O}_{13}$ is unstable and short-lived at elevated temperatures.

Table 23: Quantitative summary of attempts at synthesizing $Y_2Si_2O_7$, Y_2SiO_5 and $Y_{4.66}Si_3O_{13}$.

Sample	Target	Expt	Treatment	% $Y_3Al_5O_{12}$	% $Y_2Si_2O_7$	% $Y_{4.67}Si_3O_{13}$	% Y_2SiO_5	% Y_2O_3	% SiO_2
$Y_2O_3 + 2SiO_2$	$Y_2Si_2O_7(\gamma)$	0679c	1300°C/100 h	-	91(γ) + 9(β)	-	-	-	-
$Y_2O_3 + 2SiO_2$	$Y_2Si_2O_7(\alpha)$	0605	1550°C/36h	-	100(γ)	-	-	-	-
$Y_2O_3 + 2SiO_2$	$Y_2Si_2O_7(\delta)$	0675	1600°C/12h	-	9(γ) + 91(δ)	-	-	-	-
$Y_2Si_2O_7(\gamma)$	$Y_2Si_2O_7(\delta)$	0676	1600°C/12h	-	98(δ)	2	-	-	-
$Y_2Si_2O_7(\delta)$	$Y_2Si_2O_7(\delta)$	0678	1600°C/12h	-	100(δ)	-	-	-	-
$Y_2Si_2O_7(\gamma)$	$Y_2Si_2O_7(\alpha)$	0660a	1100°C/500 h	-	100(γ)	-	-	-	-
$Y_2Si_2O_7(\gamma)$	$Y_2Si_2O_7(\beta)$	0631	1200°C/50h	-	100(γ)	-	-	-	-
$Y_2Si_2O_7(\gamma)$	$Y_2Si_2O_7(\beta)$	0638	1200°C/100 h	-	100(γ)	-	-	-	-
$Y_2Si_2O_7(\gamma)$	$Y_2Si_2O_7(\beta)$	0660b	1200°C/500 h	-	100(γ)	-	-	-	-
$2.33Y_2O_3 + 3SiO_2$	$Y_{4.66}Si_3O_{13}$	0645	1550°C/36h	-	33(γ)	-	67(l)	-	-
$2.33Y_2O_3 + 3SiO_2$	$Y_{4.66}Si_3O_{13}$	0680	1500°C/24h	3	33(γ)	-	64(l)	-	-
$2.33(0.95Y_2O_3 + 0.05Al_2O_3) + 3SiO_2$	$Y_{4.66}Si_3O_{13}$	0681	1500°C/24h	7	40(γ)	-	53(l)	-	-
$2.33(0.90Y_2O_3 + 0.10Al_2O_3) + 3SiO_2$	$Y_{4.66}Si_3O_{13}$	0682	1500°C/24h	12	51(γ)	-	37(l)	-	-
$2.33(0.85Y_2O_3 + 0.15Al_2O_3) + 3SiO_2$	$Y_{4.66}Si_3O_{13}$	0683	1500°C/24h	17	61(γ)	-	22(l)	-	-
$Y_2O_3 + SiO_2$	Y_2SiO_5	0644	1550°C/36h	-	-	-	100(l)	-	-

4.12.3. High-Temperature X-ray Diffraction Studies of Y-Al-Si-O Systems

In-situ X-ray diffraction has been used to study phase transformations in YAS-series materials. Experiments were conducted to a maximum temperature of 1400°C.

Figure 101 shows X-ray diffraction measurements of YAS-3 as melted. Measurements were made at 50°C intervals between 1000°C and 1400°C. Formation of two phases can be observed. $Y_2Si_2O_7$ (α) (phase A) forms between 1050°C and 1300°C. $Y_2Si_2O_7$ (β) (phase B) forms from 1300°C to 1400°C.

Figure 101: High-temperature X-ray diffraction measurements of YAS-3 as melted. The sample was heated at 20°C/min between isothermal measurements at 50°C intervals. Formation of $\text{Y}_2\text{Si}_2\text{O}_7$ (α) (labeled 'A') and $\text{Y}_2\text{Si}_2\text{O}_7$ (β) (labeled 'B') can be observed.

Figure 102 shows X-ray diffraction measurements of YAS-3 as melted, held at a constant temperature of 1200°C. Measurement intervals were 360 seconds. The figure shows evolution of $\text{Y}_2\text{Si}_2\text{O}_7$ (α) for 10 hours, as evidenced by the peak at 31°2 θ , and smaller peaks around 20°2 θ . The phase reaches a constant level after around 3 hours at 1200°C.

Figure 102: X-ray diffraction measurements of YAS-3 as melted, at a constant temperature of 1200°C.

Figure 103 shows X-ray diffraction measurements of YAS-3 as melted, at a constant temperature of 1300°C. Measurement intervals were 360 seconds. Aside from $Y_3Al_5O_{12}$ and Al_2O_3 , the initial measurement shows the presence of $Y_2Si_2O_7$ (α), evidenced by the diffraction peak at 36°2 θ . This phase transforms to $Y_2Si_2O_7$ (β), which is present after cooling to room temperature.

Figure 103: X-ray diffraction measurements of YAS-3 as melted, at a constant temperature of 1300°C. The figure shows reduction in $Y_2Si_2O_7$ (α) content and an increase in $Y_2Si_2O_7$ (β) content over the duration of the experiment.

Figure 104 shows X-ray diffraction measurements of YAS-3 as melted, at a constant temperature of 1400°C. Measurement intervals were 230 seconds. $Y_2Si_2O_7$ (β) was not present at room temperature (as per measurement 0548), but was present in the first measurement at 1400°C, and for the duration of the experiment. When annealed for 100 hours at 1400C, YAS-3 formed $Y_2Si_2O_7$ (γ), as per measurement 0551. The (β) to (γ) transformation therefore occurs between 10 and 24 hours at 1400°C.

Figure 104: X-ray diffraction measurements of YAS-3 as melted, at a constant temperature of 1400°C. No change in the content of $Y_2Si_2O_7$ (β) is observed over the two hour duration of the experiment.

Figure 105 shows X-ray diffraction measurements for YAS-1 as melted, heated to 1400°C. Measurement intervals were 20 minutes. Although the YAS-1 sample annealed at 1200°C did show the crystallization of additional phases, poor peak intensities did not allow identification of any crystallization product by the Rietveld refinement in this experiment.

Figure 105: X-ray diffraction measurements of YAS-1, heated to 1400°C. Measurement intervals at 1400°C were 20 minutes.

Figure 106 shows X-ray diffraction measurements for YAS-2 as melted, at 1400°C. Measurement intervals were 20 minutes. $\text{Y}_2\text{Si}_2\text{O}_7$ (β) (labeled 'new phase') crystallizes between the first 10°C measurement and the first 1400°C measurement. This is in contrast to the YAS-2 sample annealed at 1400°C for 100 hours, which exhibited $\text{Y}_2\text{Si}_2\text{O}_7$ (γ), as per measurement 551. The (β) to (γ) transformation therefore occurs between 10 and 100 hours at 1400°C.

Figure 106: X-ray diffraction measurements of YAS-2 as melted, at a constant temperature of 1400°C. Formation of $\text{Y}_2\text{Si}_2\text{O}_7$ (β), labeled 'new phase' occurs between room temperature and the first 1400°C measurement.

Figure 107 shows a HTXRD measurement of a sample containing predominantly $\text{Y}_2\text{Si}_2\text{O}_7$ (α), prepared by B. Harlan using sol gel synthesis. The figure clearly shows conversion of (α) to (β) as temperature is increased from 1200°C to 1400°C. Cristobalite also is formed, the result of a SiO_2 excess in the precursor powder.

Figure 107: HTXRD analysis of $\text{Y}_2\text{Si}_2\text{O}_7$ (α) to (β) conversion.

4.12.4. Structure Solution of $\text{Y}_2\text{Si}_2\text{O}_7$ (α)

$\text{Y}_2\text{Si}_2\text{O}_7$ (α) was formed by the graduate student by firing sol-gel precursor at 1100°C for 16 hours. The sample also contains Y_2SiO_5 and an additional unknown phase.

$\text{Y}_2\text{Si}_2\text{O}_7$ (α) has a triclinic crystal structure with the space group P1 (2). The sample is isostructural to $\text{Tm}_2\text{Si}_2\text{O}_7$ (ICSD #413183) [4]. Tm^{3+} is almost identical in size to Y^{3+} . The crystal structure is described in Table 24. As the available sample was not phase-pure, powder density and thermal expansion data have not been measured. Figure 108 shows a Rietveld refinement of the impure $\text{Y}_2\text{Si}_2\text{O}_7$ (α) sample.

Table 24: Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (P-1) (α) polymorph, isostructural to $\text{Tm}_2\text{Si}_2\text{O}_7$ as per Hartenbach et al.[4]

S. G.		P-1(2)					
a / Å		6.59					
b / Å		6.64					
c / Å		12.02					
α / °		94.6					
β / °		90.0					
γ / °		91.8					
Volume / Å ³		524.7					
Cell ρ / gcm ⁻³		4.389					
Site	Np	x	y	z	Atom	Occ.	Beq.
Y1	2	0.45259	0.17011	0.88461	Y^{3+}	1	1
Y2	2	0.38426	0.40792	0.64224	Y^{3+}	1	1
Y3	2	0.12193	0.28396	0.36671	Y^{3+}	1	1
Y4	2	0.17095	0.67298	0.89149	Y^{3+}	1	1

Si1	2	0.34370	0.35220	0.11505	Si ⁴⁺	1	1
Si2	2	0.98730	0.16410	0.82536	Si ⁴⁺	1	1
Si3	2	0.87880	0.22380	0.59482	Si ⁴⁺	1	1
Si4	2	0.35690	0.87340	0.62027	Si ⁴⁺	1	1
O1	2	0.14800	0.01050	0.87510	O ²⁻	1	1
O2	2	0.11390	0.36440	0.78790	O ²⁻	1	1
O3	2	0.79940	0.20370	0.90690	O ²⁻	1	1
O4	2	0.90280	0.06510	0.69470	O ²⁻	1	1
O5	2	0.08710	0.32640	0.55190	O ²⁻	1	1
O6	2	0.72600	0.40250	0.62330	O ²⁻	1	1
O7	2	0.21370	0.92690	0.51200	O ²⁻	1	1
O8	2	0.21340	0.71570	0.68680	O ²⁻	1	1
O9	2	0.54000	0.72600	0.57540	O ²⁻	1	1
O10	2	0.42770	0.08310	0.68890	O ²⁻	1	1
O11	2	0.26500	0.41610	0.99510	O ²⁻	1	1
O12	2	0.15070	0.28700	0.18630	O ²⁻	1	1
O13	2	0.50070	0.16830	0.08090	O ²⁻	1	1
O14	2	0.49550	0.51910	0.18590	O ²⁻	1	1
O14	0	0.00290	0.01650	0.18300	O ²⁻	1	1

Figure 108: Rietveld refinement of $\text{Y}_2\text{Si}_2\text{O}_7$ prepared by sol-gel method by Bryan Harlan. Sample sintered at 1100°C for 16 hours. $\text{Y}_2\text{Si}_2\text{O}_7$ (alpha) structure detailed in Table 24. Sample also contains Y_2SiO_5 (P121/c1) and an additional unidentified phase.

4.12.5. Structure Solution of $\text{Y}_2\text{Si}_2\text{O}_7$ (β)

$\text{Y}_2\text{Si}_2\text{O}_7$ (β) was formed through the heat treatment of $\text{Y}_2\text{Si}_2\text{O}_7$ (α), as shown in Figure 109. This sample was used for thermal expansion and structure calculation. $\text{Y}_2\text{Si}_2\text{O}_7$ (β) features a monoclinic structure with space group C12/m1 (12). This structure has been published previously (ICSD #281313) [5]. This structure is shown in Table 25. Figure 109 shows a Rietveld refinement of a high-temperature X-ray diffraction measurement. An alternative structure that is isostructural to that of $\text{Er}_2\text{Si}_2\text{O}_7$ (ICSD #86148) [5] provides a statistically-equivalent match, as shown in Figure 110. This structure is detailed in Table 26.

Table 25: Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (C12/m1) (β) polymorph, isostructural to $\text{Er}_2\text{Si}_2\text{O}_7$, as per Redhammer and Roth. [5]

S. G.		C12/m1 (12)					
a / Å		6.8689					
b / Å		8.9638					
c / Å		4.7187					
$\gamma / ^\circ$		101.79					
Site	Np	x	y	z	Atom	Occ.	Beq.
Y1	4	0.50000	0.19363	0.50000	Y^{3+}	1	1
Si1	4	0.21800	0.00000	0.91340	Si^{4+}	1	1
O1	4	0.38030	0.00000	0.21600	O^{2-}	1	1
O2	2	0.00000	0.00000	0.00000	O^{2-}	1	1
O3	8	0.23620	0.14980	0.73240	O^{2-}	1	1

Table 26: Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (C12/m1) (β) polymorph, as per Chi et al.[6].

S. G.		C12/m1 (12)					
a / Å		6.8691					
b / Å		8.960					
c / Å		4.7168					
$\gamma / ^\circ$		101.730					
Site	Np	x	y	z	Atom	Occ.	Beq.
Y1	4	0.00000	0.30621	0.00000	Y^{3+}	1	1
Si1	4	0.21759	0.00000	0.41320	Si^{4+}	1	1
O1	4	0.00000	0.00000	0.5000	O^{2-}	1	1
O2	2	0.3794	0.00000	0.7153	O^{2-}	1	1
O3	8	0.2357	0.14921	0.2226	O^{2-}	1	1

Figure 109: Rietveld refinement of $\text{Y}_2\text{Si}_2\text{O}_7$ (β) sample, as per structure in Table 25.

Figure 110: Rietveld refinement of $\text{Y}_2\text{Si}_2\text{O}_7$ (β) sample, as per structure in Table 26.

4.12.6. Thermal Expansion of $\text{Y}_2\text{Si}_2\text{O}_7$ (β)

The thermal expansion of $\text{Y}_2\text{Si}_2\text{O}_7$ (β) was calculated using high-temperature X-ray diffraction. The phase exhibits anisotropic thermal expansion, as shown in Figure 111. Thermal expansion

values were fitted using a cubic function. Parameters are shown in Table 27. Calculated linear CTE values, between 20°C and 1200°C, are shown in Table 28.

Figure 111: Thermal expansion of $\text{Y}_2\text{Si}_2\text{O}_7$ (β)

Table 27: Parameters for cubic function ($dL/L = y_0 + dx + ex^2 + fx^3$) fitted to thermal expansion values

axis	d	e	f	y_0
a	1.733e-6	3.644e-9	-2.691e-13	-2.743e-5
b	9.715e-7	3.485e-9	-8.026e-13	7.845e-6
c	-1.101e-6	3.762e-9	-1308e-12	4.715e-5
Vol	-7.280e-7	1.475e-8	-4.182e-12	2.115e-5

Table 28: Linear coefficients of thermal expansion for $\text{Y}_2\text{Si}_2\text{O}_7$ (β), calculated between 20°C and 1200°C

a	$5.8 \times 10^{-6} \text{ K}^{-1}$
b	$4.6 \times 10^{-6} \text{ K}^{-1}$
c	$1.8 \times 10^{-6} \text{ K}^{-1}$
vol	$4.2 \times 10^{-6} \text{ K}^{-1}$

4.12.7. Structure Solution of $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$

$\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$ was prepared in phase-pure form by sintering mixed oxides at 1550°C for 36 hours, as per measurement 0605. $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$ has a monoclinic crystal structure with space group P1121/b (14). The phase is isostructural to $\text{Er}_2\text{Si}_2\text{O}_7$ (ICSD #28190) [7]. Powder density and thermal expansion were measured. The structure is shown in Table 29. Figure 112 shows a Rietveld refinement of phase-pure $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$.

Table 29: Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (P1121/b) (γ) polymorph, isostructural to $\text{Er}_2\text{Si}_2\text{O}_7$ as per Smolin and Shepelev.[7].

S. G.		P1121/b (14)					
a / Å		4.6885105 ± 0.0005125					
b / Å		5.5825408 ± 0.0002403					
c / Å		10.8408035 ± 0.0002569					
$\gamma / ^\circ$		96.03415 ± 0.00225257					
Cell Volume / Å ³		282.23					
GOF		2.75					
Rwp		10.856					
Cell Density / gcm ⁻³		4.072					
Powder Density / g cm ⁻³		4.1169 ± 0.0013					
Site	Np	x	y	z	Atom	Occ.	Beq.
Y1	4	0.88829	0.09318	0.34934	Y ³⁺	1	1
Si1	4	0.36010	0.64420	0.38710	Si ⁴⁺	1	1
O1	2	0.50000	0.50000	0.50000	O ²⁻	1	1
O2	4	0.20520	0.86530	0.44860	O ²⁻	1	1
O3	4	0.12350	0.45830	0.31010	O ²⁻	1	1
O4	4	0.61840	0.75220	0.29840	O ²⁻	1	1

Figure 112: Rietveld refinement of phase-pure $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$.

4.12.8. Thermal Expansion of $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$

Thermal expansion of $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$ was measured using high-temperature X-ray diffraction. The phase exhibits anisotropic thermal expansion, with the c-axis having a CTE close to zero, as shown in Figure 113. Thermal expansion values were fitted using a cubic function. Parameters are shown in Table 30. Calculated linear CTE values, between 20°C and 1200°C, are shown in Table 31.

Figure 113: Thermal expansion of $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$

Table 30: Parameters for cubic function ($dL/L = y_0 + dx + ex^2 + fx^3$) fitted to thermal expansion values

axis	d	e	f	y_0
a	1.124e-4	2.619e-9	-1.012e-12	2.227e-5
b	3.146e-6	2.131e-9	-5.052e-13	-8.702e-5
c	4.556e-6	9.789e-10	7.814e-15	-1.031e-4
Vol	2.029e-6	2.113e-9	-5.876e-13	-4.832e-5

Table 31: Linear coefficients of thermal expansion for $\text{Y}_2\text{Si}_2\text{O}_7(\gamma)$, calculated between 20°C and 1200°C

a	$0.6 \times 10^{-6} \text{ K}^{-1}$
b	$5.0 \times 10^{-6} \text{ K}^{-1}$
c	$5.8 \times 10^{-6} \text{ K}^{-1}$
vol	$3.8 \times 10^{-6} \text{ K}^{-1}$

4.12.9. Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (δ)

$\text{Y}_2\text{Si}_2\text{O}_7$ (δ) was prepared in phase-pure form by sintering phase-pure $\text{Y}_2\text{Si}_2\text{O}_7$ (γ) at 1600C for 12 hours, as per measurement 0678. $\text{Y}_2\text{Si}_2\text{O}_7$ (δ) has an orthorhombic crystal structure, with space group Pnam (62). This structure has been published previously by Diaz et al. (ICSD #33721) [8]. The structure is shown in Table 32. Figure 114 shows a Rietveld refinement of phase-pure $\text{Y}_2\text{Si}_2\text{O}_7$ (δ) using this structure. Thermal expansion has not been measured for this phase.

Table 32: Structure of $\text{Y}_2\text{Si}_2\text{O}_7$ (Pnam) (δ) polymorph, as per Diaz et al. [8].

S. G.		Pnam (62)					
a / Å		13.665					
b / Å		5.016					
c / Å		8.139					
Cell Density / gcm ⁻³		4.12					
Powder Density / gcm ⁻³							
Site	Np	x	y	z	Atom	Occ.	Beq.
Y1	8	0.1255	0.3395	-0.0096	Y ³⁺	1	1
S1	4	0.3179	0.3711	0.25	Si ⁴⁺	1	1
Si2	4	0.5410	0.6214	0.25	Si ⁴⁺	1	1
O1	8	0.2671	0.4875	0.0861	O ²⁻	1	1
O2	4	0.3476	0.0613	0.25	O ²⁻	1	1
O3	4	0.4218	0.5588	0.25	O ²⁻	1	1
O4	8	0.5477	0.7994	0.0817	O ²⁻	1	1
O5	4	0.6031	0.3386	0.25	O ²⁻	1	1

Figure 114: Rietveld refinement of $\text{Y}_2\text{Si}_2\text{O}_7$ (δ)

5. Conclusions

Extensive understanding of the relations between glass composition and the behavior of the sealants has been gained thus far in the project. The effort of two postdoctoral fellows and one graduate student, plus the faculty and team members at GE, has kept the project on schedule.

The SOFC sealants are currently fully characterized in terms of crystallization, bulk glass viscosity, TEC, and wetting. The remaining work will focus on glass-ceramic viscosity, cell-level testing, and electrical/environmental degradation. A full designed experiment, consisting of 13 glasses, has been completed, and several additional glasses were prepared to optimize specific properties. Detailed comparisons of the fundamental behavior of the new designed glasses with the “known” technology of the PNNL G18 published sealant, are essentially complete.

The compositional design work has focused on reducing the sensitivity of the sealant to wet hydrogen. Of course, the compositional changes affect the critical parameters of viscosity, TEC, crystalline phases formed, etc. However, the project has been highly successful in producing test vehicles with acceptable leakage behavior. Work to date has provided a range of sealants with varying physical properties, and has demonstrated that even the more refractory glasses can form high quality seals if the appropriate parameters of time, temperature, and load are employed during the sealing cycle.

Ultimately, the project will conclude with final degradation testing to evaluate how the new glass compositions perform in comparison with the base EG9207 glass and the known PNNL G18 glass. Regardless of the degradation behavior outcomes, a full property – performance matrix will be completed, which will be used to guide further development of the technology. Of critical importance is the delicate balance between the glass composition and the exacting requirements of large-volume production on the specific properties of the sealants.

The nature of the work related to sealants for lighting has a slightly different focus, that is, to understand the behavior of a limited portion of the rare earth – alumina – silica phase diagram. Extensive phase equilibria work has resulted in the discovery or refinement of 4 new phases in the system, and all of the new phases have been characterized for their anisotropic thermal expansion behavior. A large amount of phase stability information has been obtained, and the thermal expansion of the bulk sealant has been measured for the three target compositions. Preliminary functional lamp testing has been conducted and will continue through year 2 of the contract. Analyses of the lamps are on-going and will be described in the final report. The work to date has provided an enormous body of fundamental experimental knowledge that was previously unknown. Further development of the technology is expected to focus on incorporation of the new experimental data into computer modeling efforts and additional experimental studies that can be used to optimize the lamp processing conditions for improved performance.

6. References

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7. List of Acronyms and Abbreviations

1. EBSD Electron backscattered diffraction
2. G18 Designation for the published PNNL SOFC sealing glass
3. HTXRD High temperature X-ray diffraction
4. ICP Inductively coupled plasma atomic emission spectroscopy
5. ICSD Inorganic crystal structure database
6. PDF Powder diffraction file
7. PNNL Pacific Northwest National Laboratory
8. SEM Scanning electron microscope
9. TEC Thermal expansion coefficient
10. YA yttrium aluminate
11. YAS yttrium aluminosilicate
12. YAG Yttrium aluminum garnet, $Y_3Al_5O_{12}$
13. XRD X-ray diffraction

8. Appendices

None