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Evaluating the Microwave Heating of Spinel Crystals in High-Level Waste Glass

J. H. Christian

A. L. Washington

August 2015

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EXECUTIVE SUMMARY

Spinel ($A^{2+}B^{3+}{}_2O^{2-}{}_4$) crystallization in a high-level waste (HLW) glass melter can negatively affect melter operations. However, significant crystal accumulation can be avoided by diluting spinel forming precursors with glass forming chemicals, thus operating the melter above the liquidus temperature of the glass melt. However, these mitigation strategies can limit waste loading below what might otherwise be acceptable for processing and product performance.

One method, which has yet to be explored in limiting spinel crystal accumulation within a melter, is the use of microwave irradiation to selectively heat and dissolve crystals (that are allowed to form) while not significantly affecting the temperature of the non-microwave absorptive glass. In the same manner that the melter electrodes exploit the resistive nature of glass to induce Joule heating, microwave radiation can exploit the polar nature of spinel crystals to induce microwave heating without the need for an external microwave susceptor.

In this report, the microwave heating of a crystal-free and a partially (24 wt%) trevorite-crystallized waste glass simulant were evaluated. The results show that a 500 mg piece of partially crystallized waste glass can be heated from room-temperature to above 1600 °C (as measured by infrared radiometry) within 2 minutes using a single mode, highly focused, 2.45 GHz microwave, operating at 300 W. X-ray diffraction measurements show that the partially crystallized glass experiences an 87 % reduction in trevorite following irradiation and thermal quenching. When a crystal-free analogue of the same waste glass simulant composition is exposed to the same microwave radiation it could not be heated above 450 °C regardless of the heating time.

The crystal reduction achieved by selectively heating spinels in the presence of glass suggests that microwave specific heating should be further explored as a technique for preventing spinel accumulation at the bottom of a HLW melter and/or glass discharge riser if crystals are allowed to form for the sake of achieving a higher volume fraction of waste incorporation.

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LIST OF ABBREVIATIONS

DWPF	Defense Waste Processing Facility
DOE	U.S. Department of Energy
EPR	Electron Paramagnetic Resonance
HLW	High-Level Waste
IR	Infrared
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

1.0 Introduction

Joule-heated melters are the preferred melter technology for HLW immobilization in the DOE complex. At the Defense Waste Processing Facility (DWPF), HLW is melted with a glass frit inside a Joule-heated ceramic melter. A significant limitation to higher waste loadings in waste glasses at both DWPF and the Hanford Tank Waste Treatment and Immobilization Plant (WTP) is the formation of spinel crystals ($A^{2+}B^{3+}{}_2O^{2-}{}_4$), which can negatively affect melter operations in several ways. The resistivity and viscosity of the glass melt are two of the most important properties for controlling the vitrification process.[1] Crystallization in the melt pool can increase the viscosity of the melt, thereby making it difficult to pour through the riser.[2] Additionally, a low viscosity melt can cause erosion to the refractory and melter components. Furthermore, the resistivity of waste glass is optimum between 1 and 10 Ω-cm. In this range, glass is conductive enough to pass electric currents without requiring high voltages, but is not conductive enough that excessive current densities are required at the electrodes to produce heat.[1] The formation of spinel crystals in the melter can alter the resistivity of the melt and impact the ability to generate heat and control the melt temperature. Additionally, spinels can accumulate at the bottom of a melter and/or partially or completely block the pour spout, since the density of spinel crystals (~5.2 g/mL)[3] is more than twice as high as that of typical borosilicate waste glass (~ 2.6 g/mL).[4] Significant crystal accumulation in the melter can cause an electrical short that prohibits heating of the melt pool.

Spinel accumulation in the melter is avoided by diluting waste components with glass forming chemicals although this dilution strategy limits waste loading below what might otherwise be acceptable for processing and product performance.[5] The effect of this dilution is to maintain a glass composition with soluble chromium and a liquidus temperature that is below the melter operating temperature. Despite the potentially negative effects of spinel crystallization within a HLW melter, tolerating the formation of some spinel crystals, that do not have an impact on the glass durability performance, would provide access to higher waste loadings.[6] However, the crystals would need to be continuously or periodically removed so that the viscosity and conductivity of the glass are not drastically altered, and so that other problems associated with accumulation, such as riser and pour spout blockage, would not occur.

Heat is an excellent way to prevent and dissolve crystals in the melt pool. However, it can be difficult if not impossible to heat a settled layer of spinel crystals via Joule heating of the glass melt due to the high melting point of spinel. In summation, while a crystal-tolerant approach to glass processing would increase waste loadings, which in turn could provide cost savings and speed up the completion of DOE waste missions, the currently used melter technology is not equipped to operate long-term in a crystal-tolerant environment.

Fortunately, there may be other ways to dissolve crystals within the melter. One such way is microwave heating. While Joule heaters exploit the resistive nature of glass to generate heat, microwave radiation exploits the polar nature of crystalline solids to induce dielectric heating. Microwave heating is, therefore, poorly suited for heating most glasses, but is excellent at heating polarizable materials.[7] Thus, microwave heating appears to be useful for generating sufficiently high temperatures in partially crystallized glass, and may be capable of targeting and generating heat specifically at spinel crystalline sites in a glass matrix. Herein microwave heating of partially (24 wt%) trevorite-crystallized waste glass simulant is evaluated.

2.0 Experimental Procedure

2.1 Glass Composition Selection

A HLW simulant glass, identified as SP-TRV, was selected for this study due to its amorphous structure when thermally quenched, and its propensity to generate trevorite during a single 24 h heat treatment at 850 °C. This allowed for the study of microwave heating of both a crystal-free and crystallized waste glass simulant with the same composition, thus eliminating compositional variability from the study. The SP-TRV composition is provided in Table 2-1.

Table 2-1. Target Composition of SP-TRV in Weight Percent

Batch Component	Wt% Oxide
Al_2O_3	7.86
B_2O_3	7.65
CaO	0.54
CdO	0.62
Cr_2O_3	0.16
Fe_2O_3	17.55
K_2O	0.32
Li_2O	1.91
MnO	0.33
Na_2O	17.87
NiO	1.50
P_2O_5	0.31
SiO_2	38.59
ZrO_2	3.98
Ce_2O_3	0.19
La_2O_3	0.21
MoO_3	0.12
Nd_2O_3	0.17
SnO_2	0.10
Sum:	99.98[a]

2.2 Glass Fabrication

SP-TRV was prepared from the proper proportions of reagent-grade metal oxides, carbonates, boric acid, and salts in a 200 g batch. The raw materials were mixed and placed into a 250 mL platinum/gold crucible. A lid was placed on top of the crucible to prevent contamination from furnace refractory and dust particles. The batch was placed into a high-temperature furnace at the target melt temperature of 1150 °C. The crucible was removed from the furnace after an isothermal hold at the melt temperature for 1 h.

[a] The original composition suggested by J. Matyáš of Pacific Northwest National Laboratory included 0.02 wt% F, which was not included in the glass fabricated for this study.

The glass was then poured onto a clean, stainless steel plate and allowed to air cool (quench). The quenched glass was evaluated using powder X-ray diffraction (XRD) to confirm an amorphous glass structure (see Section 2.4.1). A portion of the glass was then ground and well-mixed using an agate mill. The resultant powder was placed in a furnace at 850 °C for 24 h to induce spinel crystallization. The crystallinity of the sample was confirmed via XRD. The amorphous and crystallized glasses were used as the stock for the microwave studies described herein.

2.3 Microwave Equipment

A single mode, 2.45 GHz, CEM Discover-SP model microwave reactor with variable power options was used in this study (Figure 2-1).

2.4 Property Measurements

2.4.1 X-ray Diffraction

Quenched, heat treated, and microwave irradiated samples were measured using XRD to quantify any crystallization. The samples were ground in an agate mortar and pestle to reduce the particle size and to homogenize the samples. The ground powder was placed on a glass slide. A few drops of a 10% Amyl Acetate/Collodion solution was added to the ground powder to fix the powder to the glass slide.

The data were collected on a Bruker D8 X-ray Diffractometer by step scanning over a 2θ range of 5-70° with a step size of 0.02° and a dwell time of 1 s. All the instrument parameters are listed in Table 1. Search-match identification of all the phases was performed with Jade software (Version 2010) from Materials Data Inc. combined with the PDF-4 database from the International Centre for Diffraction Data. A CaF_2 intensity standard was measured with the glass and was used to quantify the wt% of the crystalline phase in the glass. The utilized measurement conditions provided a 0.5 wt% detection limit. A broad hump(s) in XRD data was considered to represent an X-ray amorphous, glassy sample.

Table 2-2. XRD Instrument Parameters

Radiation Source	CuKα X-ray
Source Power	45 kV, 40 mA
Wavelength	1.5405982 Å
2θ Range	$5^{\circ} - 70^{\circ}$
Step Interval	0.02° (2θ)

2.4.2 Infrared Temperature Measurements

Accurate temperature measurements inside of a microwave reactor are a non-trivial task since the electromagnetic field of the microwaves will influence most traditional methods of temperature measurements (e.g. thermocouples or thermometers). Herein the glass temperature during microwave irradiation was monitored using a FLIR SC645 model infrared (IR) camera. The camera was mounted at the top of the microwave reactor in order to observe the microwave reactor cavity during heating. The microwave and IR camera set up is shown in Figure 2-1 and the IR camera specifications are listed in Table 2-3.

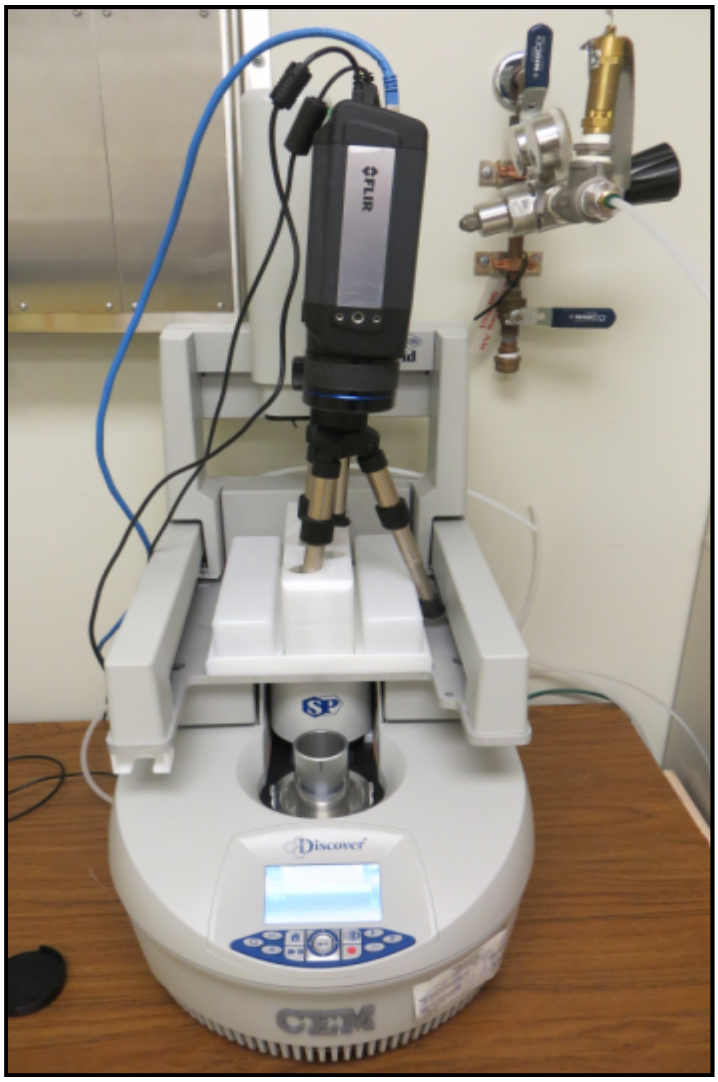

Figure 2-1. The CEM microwave reactor and IR camera configuration.

Table 2-3. FLIR SC645 Model Specifications

Focal length	24.6 mm
Spatial resolution (IFOV)	0.69 mrad
IR resolution	640 x 480 pixels
Measurement temperature range	-20 ℃ to 2000 ℃
Accuracy	± 2 °C or ± 2% of reading
Operating temperature range	-15 ℃ to + 50 °C

3.0 Results and Discussion

XRD measurements of the quenched and heat-treated SP-TRV glass composition showed an amorphous and a trevorite-crystallized structure, respectively, as shown in Figure 3-1. Trevorite crystallization was quantified at a concentration of 24 wt% in the glass. A photo of a non-crystallized and partially crystallized piece of SP-TRV is shown in Figure 3-2. In this figure, it can be seen that the presence of trevorite in the glass matrix causes the glass to possess a dull, brown-red color, while the non-crystallized glass is black and shiny

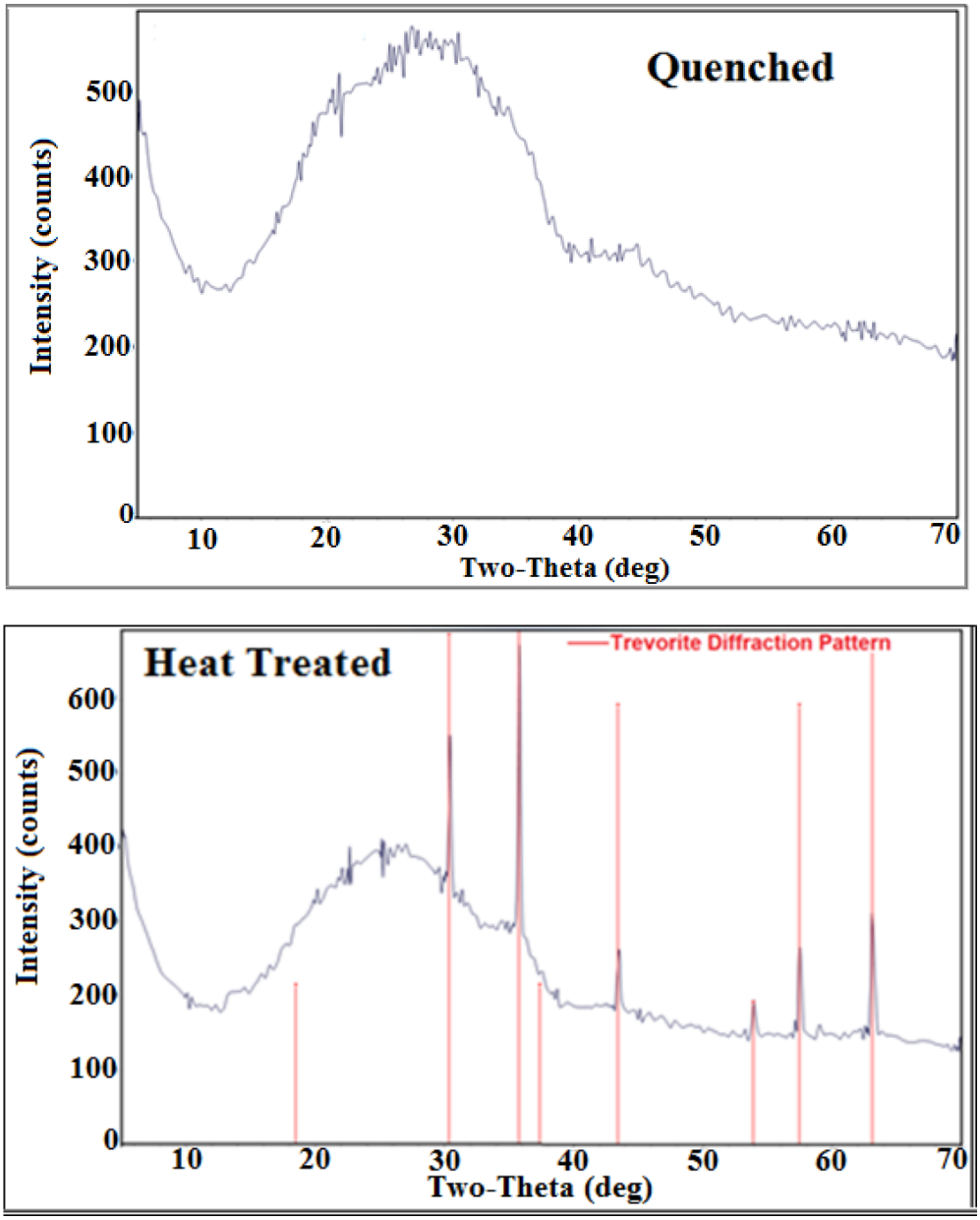

Figure 3-1. X-ray Diffraction patterns of SP-TRV glass composition formed by (top): rapid thermal quenching on a stainless steel plate and (bottom) 24 hr. heat treatment at 850 °C.

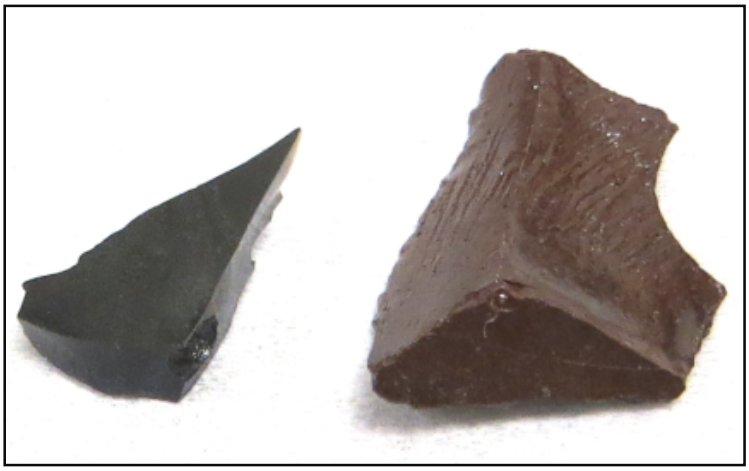

Figure 3-2. A photo of non-crystallized (left) and partially crystallized (right) SP-TRV waste glass simulant.

When a 500 mg piece of the non-crystallized glass was irradiated inside the microwave cavity, the glass immediately began to heat at approximately 1.3 ℃/sec until reaching approximately 100 °C. Above 100 °C the heating occurred even slower, at a rate of approximately 0.5 °C/sec until reaching approximately 450 °C. At this point, the glass stopped heating, but maintained its temperature around 400 °C - 450 °C. Despite being continuously irradiated at a fixed 300 W microwave power for over twenty minutes, the glass never reached temperatures greater than 450 °C. Similar results were observed on multiple samples, although the extent of heating and the initial heating rate showed some variation. In fact, some samples could only be heated to around 100 °C - 200 °C regardless of irradiation time. IR images of a sample that reached approximately 450 ℃ are shown as a function of the irradiation time in Figure 3-3.

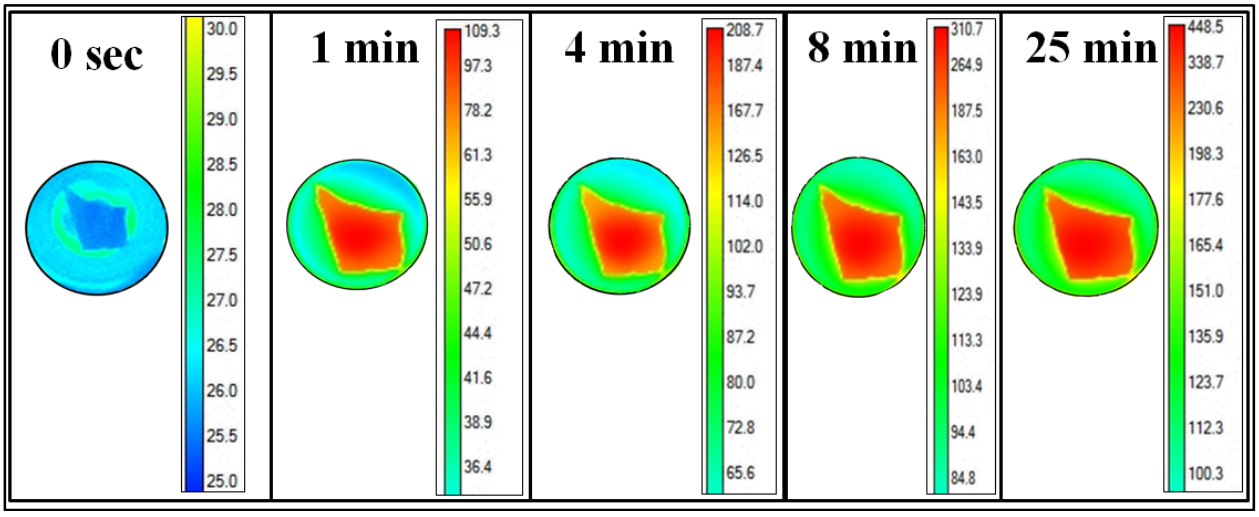

Figure 3-3. IR radiometry images of non-crystalline SP-TRV glass under microwave irradiation for different amounts of time. The glass is the shapeless object at the center of the circular image. The temperature bar is in °C. The temperature of the glass ultimately plateaus around 450 °C

Since a truly amorphous glass should show little to no dielectric heating due to the lack of electric polarizability, the heating observed in SP-TRV is tentatively ascribed to the dielectric loss of the many metals within the glass and the existence of more highly ordered regions in glass, referred to as clusters or quasicrystals. These clusters often have atomic arrangements that approach those of crystals[8,9], however, they do not possess long-range ordering like crystalline solids.

The dielectric heating of a 500 mg monolith of the trevorite-crystallized analogue of SP-TRV occurred faster and reached higher temperatures than the non-crystallized version. Although some variation in the heating rate and maximum temperature was seen from sample to sample, generally the samples heated at a rate of approximately 15 °C /sec from room temperature to approximately 400 °C. Above 400 °C the samples rapidly heated at a rate of approximately 20 °C /sec. IR radiometry showed that temperatures for these samples reached as high as 1600 °C after only 2 minutes and that the heating rate generally slowed down in the high temperature range, although there was variation among different samples. Importantly, the microwave power appears to be an important factor in the heating rate. Cursory measurements at 50W, 100W, and 200W microwave power, showed that different heating rates can be achieved through variation of the microwave power, although these results have not been quantified at this stage. This result demonstrates the ability to use power to control the temperature of a partially crystallized, glassy material being heated by microwaves. IR images of a typical sample are shown as a function of the irradiation time in Figure 3-4.

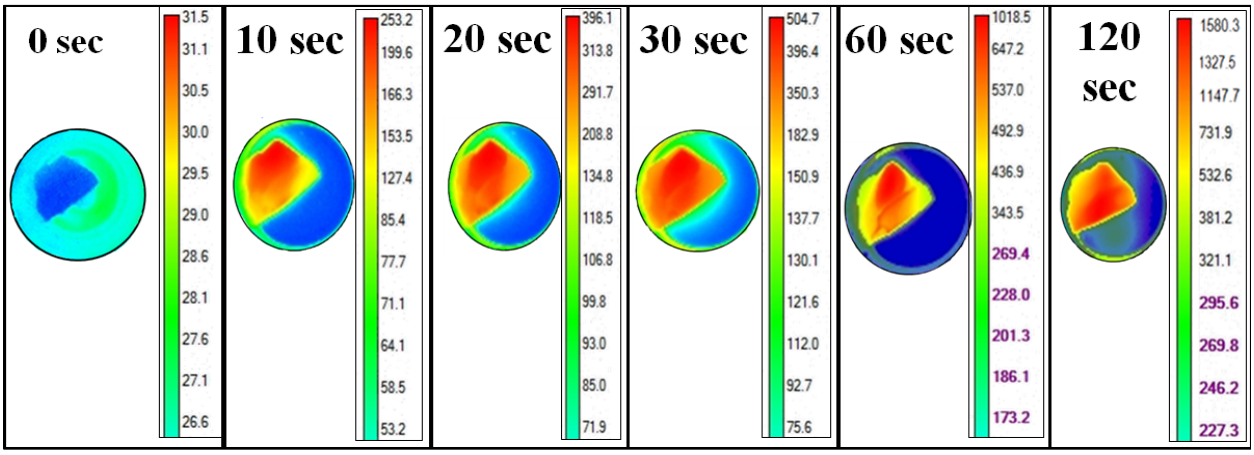

Figure 3-4. IR radiometry images of a partially crystallized piece of SP-TRV composition glass under microwave irradiation for varying amounts of time. The glass is the shapeless object at the center of the circular image. The temperature bar is in °C. The glass can be seen melting and changing shape after one minute as the temperature rises above 1000 °C.

The rapid increase in the heating rate above 400 °C is likely due to the nature of the radiometry measurements. Specifically, IR radiometry primarily measures the temperature at the surface of the glass; however, microwaves will penetrate to a certain depth within a material, known as the penetration depth, which is formally defined as the depth at which the electromagnetic radiation power density has decreased to 37% of its initial value at the material's surface.[10] Thus, microwave heating occurs "from the inside out" (volumetric heating) as opposed to conventional heating methods that heat "from the outside in" through surface heat dissipation into the bulk.[7] Therefore, IR radiometry is not adequate for determining the bulk temperature of a glass until the glass begins to soften and the hot core becomes

exposed, which is likely why the temperature rapidly increases once the surface is measured as 400 °C. The variance in heating rate and maximum temperature amongst different samples is likely due to small variations in the ratio of glass to trevorite present in each sample.

After being irradiated for 2 minutes, these samples were cooled and visually inspected. Not only did the microwave heating cause the crystallized glass to melt, but the samples were noticeably transformed from dull and reddish brown to shiny and black, and were similar in appearance to the non-crystalline version of the glass. The glass is shown before and after irradiation in Figure 3-5. Additionally, when previously melted samples were placed back inside the microwave cavity for further irradiation, the samples exhibited poor heating similar to the heating seen in non-crystalline SP-TRV. XRD measurements of samples, following 2 minutes of irradiation and heating, showed a trevorite concentration of 3.1 wt%, which is an 87.1 % decrease from the starting material. This result suggests that only 2 minutes of microwave exposure was sufficient to dissolve most of the trevorite in the glass matrix. Additionally, through rapid cooling, the sample was kinetically prohibited from reforming trevorite, thus the sample exhibited poor reheating.

Importantly, older studies on microwave processing of simulated nuclear waste glasses[11] and fusion of melter feed[12] have employed microwave susceptors like silicon carbide in order to generate heat for glass and melter feed. These susceptors or "getters" interact strongly with microwave radiation and get very hot. Heat is then transferred from the susceptor to the surrounding environment (which does not experience strong microwave heating) without bias. Thus, the heat does not target specific components like crystals in a glass matrix. The lack of specificity in this type of heating can cause glass to become too hot and radionuclide volatilization can occur. These complications are likely to be avoided when crystal-specific heating without an external susceptor is employed. As was shown above, trevorite crystals are excellent microwave absorbers, and they can dissolve in glass during irradiation. Thus, they cannot be continuously heated under irradiation. In essence, having a dissolving microwave absorber may be thought of as a built in safety feature that prohibits excessive temperatures from being reached in the irradiated environment.

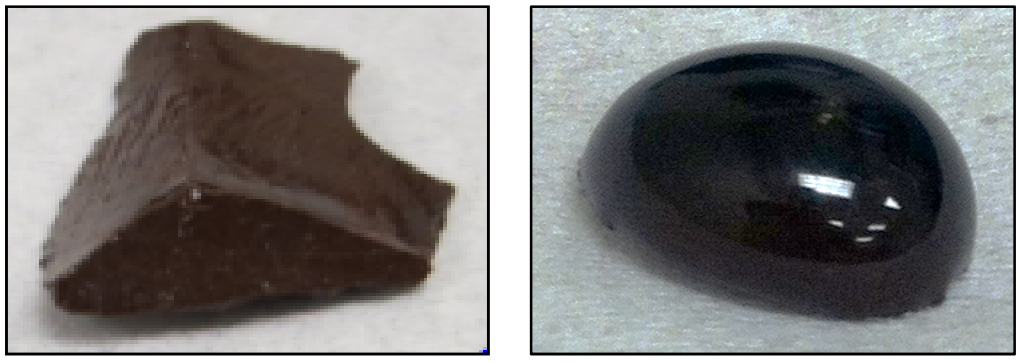

Figure 3-5. Photographs of partially crystallized SP-TRV glass composition before (left) and after (right) 2 minutes of microwave irradiation.

4.0 Conclusions and Path Forward

Microwave heating of partially crystallized HLW glass simulants was shown to be capable of inducing rapid heating to temperatures around 1600 °C as evidenced by in-situ IR radiometry measurements. Additionally, irradiation of non-crystallized glass simulant was only capable of inducing heat up to approximately 450 °C under the same conditions. These results suggest that microwave heating may be useful for targeting and heating spinel crystals within a HLW glass melter while preventing the glass melt pool from reaching temperatures where radionuclide volatilization becomes problematic.

At this stage it is recommended that additional experiments be carried out in order to determine whether similar heating effects can be obtained for different spinel compositions in a glass matrix, and whether these effects occur in a molten environment. That is, if spinel crystals are settled at the bottom of a molten pool of glass in the melter or in the discharge riser, and microwave irradiation is applied, can the heating occur in a similar fashion as was shown in the experiments herein where the microwave irradiation was first applied at room temperature? It is also recommended that the effects of microwave power be explored in order to better understand the heating rate of crystallized glass as a function of microwave power. An investigation should also be conducted to determine the best way to install a microwave source in a HLW melter. Lastly, the viability of using microwave radiation to quantify the amount of spinel crystals in a melter should be investigated. It may be possible to correlate the microwave radiation loss to the amount of crystals within a glass melt since the above experiments show that the dielectric loss through a non-crystalline environment is different than in a crystalline one. A diode detection system, similar to the type used to detect microwaves in Electron Paramagnetic Resonance (EPR) spectroscopy, would likely be suitable for determining the microwave radiation loss.

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