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Microwave-Specific Heating of Crystalline Species in Nuclear Waste Glass

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ABSTRACT

The microwave heating of a crystal-free and a partially trevorite-crystallized nuclear waste glass simulant were evaluated. Our results show that a 500 mg monolith of partially crystallized waste glass can be heated from room-temperature to above 1600 °C within 2 minutes using a single mode, highly focused, 2.45 GHz microwave, operating at 300 W. Using X-ray diffraction measurements we show that trevorite is no longer detectable after irradiation and thermal quenching. When a crystal-free analogue of the same waste glass simulant composition was exposed to the same microwave radiation it could not be heated above 450 °C regardless of the heating time. The reduction in crystalline content achieved by selectively heating spinels in the presence of glass suggests that microwave specific heating should be further explored as a technique for remediating crystal accumulation in a glass melt.

1. INTRODUCTION

Microwave radiation heats by fundamentally different mechanisms than conventional heat sources, and thus has been used in various applications across many disciplines since the 1940s.[1,2] Although there has often been unfounded speculation that resonant energy coupling of microwave radiation with matter can alter or reduce the activation energy of certain processes, a phenomenon often referred to as “the microwave effect”, there is no clear mechanism by which microwave radiation can alter bond changing events via energy resonance.[3,4] Thus, early reports of athermal and molecular microwave heating that significantly accelerate bond-changing events were simply flawed by inaccurate temperature measurements and a lack of appreciation for the fundamental dielectric loss processes that cause microwave heating.[3-5] Nonetheless, in many applications, the ability to focus microwaves and generate heat at selected targets has significant advantages over conventional heating methods.

Owing to the shorter reaction times and site-specific heating that is offered by microwaves, organic and inorganic microwave assisted synthesis has become more prevalent in recent years as the availability of commercial microwave equipment has increased.[6,7] In the catalyst industry, microwave specific heating of catalyst active sites has been demonstrated to enhance reactivity and afford new catalytic pathways in a variety of systems. One area where microwave specific heating has yet to be explored, but where it may hold potential, is in the melting of accumulated crystals in nuclear waste glass melters.

In the United States (U.S.), France, Japan, China, India, Russia, and the United Kingdom, high-level nuclear waste is immobilized through vitrification in glass.[8,9,10] In the United States, this vitrification currently occurs in Joule heated melters operating at 1150 °C. Although increased loading of waste components in the glass is ideal for volume reduction, mission lifetime reductions, and cost savings, the waste loading must be kept below the solubility limits of the major crystal forming waste components at the melter operating temperature.[11,12] When the solubility limits are exceeded, crystalline phases can form spontaneously via homogeneous nucleation or heterogeneous nucleation on insoluble noble metal sites within the waste.[13] The formation of crystalline phases in a glass melt can cause several negative effects on vitrification operations. Specifically, crystal formation can cause viscosity changes to the melt pool, which can make it difficult to pour and discharge glass from the melter.[14] A low viscosity melt can cause erosion to the refractory and other melter components. Crystals can also cause the resistivity of glass to change, thus impacting the ability to generate and control heating in the melt pool.[15] And, significant crystal accumulation can partially or completely block the glass pour spout.

Although application of additional heat can be used for dissolving crystals precipitated from glass, routine operations limit U.S. melter temperatures to 1150 °C. The potential for radionuclide volatilization and accelerated creep of melter electrodes dictates that the upper temperature operation limit for nuclear waste glass melters in the U.S. is currently fixed at 1200 °C.[11,12,16,17] Unfortunately, this upper temperature limit is too low to dissolve spinel crystals [($A^{2+}B^{3+}{}_2O^{2-}{}_4$), where A = Fe, Ni, Mn, or Zn, and B = Fe or Cr] since these crystals have melting points well above 1200 °C.[14,18,19] Therefore, once formed in a melter, spinel crystals cannot be dissolved using fixed operational conditions. Thus, to avoid the negative effects associated with crystal accumulation in a melter, crystal formation is avoided outright by diluting waste components with glass forming chemicals. However, this dilution strategy lowers the achievable waste loading for some high-level waste streams in glass.[20]

Motivated by the prospect of achieving higher waste loadings without compromising the integrity of melter operations, we utilized microwaves to heat crystals dispersed in waste glass without significantly altering the temperature of the glass. Herein, we show for the first time, that trevorite ($NiFe_2O_4$) crystals dispersed in a nuclear waste glass simulant can be dissolved/melted by heating 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. Importantly, no external microwave susceptors were needed to achieve heating since the spinel crystals have a high cross section of absorption for microwaves and act as internal susceptors even when dispersed in a glass matrix. X-ray diffraction measurements confirm that a 24 wt% trevorite-crystallized glass can be made crystal-free through microwave irradiation and thermal quenching. Additionally, when a crystal-free analogue of the same glass composition is exposed to the same microwave radiation, we show that it cannot be heated above ~450 °C regardless of the heating time. Thus, this site-specific-heating application of microwaves seems worthy of further investigation for use in different industrial processing applications extending beyond the nuclear waste industry.

2. Experimental

2.1 Glass Composition and Fabrication

A nuclear waste glass simulant, hereafter referred to as **A-G** was selected for this study due to its amorphous structure when thermally quenched in air from 1150 °C, and its propensity to generate trevorite during a 24 h heat treatment at 850 °C. This composition allowed us to study the microwave heating of both a crystal-free and partially crystallized waste glass simulant of the same chemical composition, thus eliminating compositional variability from our study. **A-G** was prepared from the proper proportions of reagent-grade metal oxides, carbonates, boric acid, and salts in a 200 g batch. The composition of **A-G** is provided in Table 1. Raw batch 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 then placed into a high-temperature furnace at the targeted melt temperature of 1150 °C. The crucible was removed from the furnace after an isothermal hold of 1 h. The glass was then poured onto a clean, stainless steel plate and allowed to air cool (quench). A portion of the glass was then ground and well-mixed using an agate mill. The resultant powder was placed in a platinum/gold crucible inside a furnace at 850 °C for 24 h to induce spinel crystallization. The crystallinity of all samples was confirmed via XRD (see below).

2.2 X-ray Diffraction

Quenched, heat treated, and microwave irradiated samples were measured using XRD to quantify any crystallization. For heat treated samples, settling of crystals in the glass during heat treatment makes representative sampling a challenge. Thus, when obtaining samples for XRD measurements we cut cross sections from the glass that contained the top, bulk, and bottom of the glass, thereby representing typical pieces that would be used for microwave heating experiments. 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 were added to the ground powder to fix the powder to the glass slide. The data were collected on a Bruker D8 Discover X-ray Diffractometer (using a Cu Kα $\lambda = 1.5406$ Å) by step scanning over a 2θ range of 5-70° with a step size of 0.02° and a dwell time of 1 s. Search-match identification of all the phases was performed with Jade software (Version 2010) from Materials Data Inc.[21] combined with the PDF-4 database from the International Centre for Diffraction Data.[22] A CaF_2 intensity standard purchased from Sigma Aldrich 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.

2.3 Microwave Irradiation

All heating was performed in a single mode, CEM Discover-SP model microwave reactor operating at 300 W and 2.45 GHz. Heating was carried out in static 35 mL quartz vessels. After irradiation, hot vessels were cooled using high pressure air (40 psi).

2.4 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).[3,23,24] Thus, the glass temperature during microwave irradiation was monitored using a FLIR SC645 model infrared (IR) camera capable of measuring a temperature range of -20 °C to 2000 °C with a temperature accuracy of 2%. The camera had a 24.6 mm focal length, 0.69 mrad spatial resolution, a spectral range of 7.5 - 14 μm, and was mounted at the top of the microwave reactor in order to observe the microwave reactor cavity during heating. IR radiometry primarily measures the temperature at the surface of the glass due to poor IR transmission into the bulk; however, bulk temperature measurement accuracy improves when the glass surface begins to melt.[25]

3. Results and Discussion

XRD measurements of thermally quenched **A-G** (Fig. 1 left) showed a broad hump, which is typical of an amorphous glass material.[12] Measurements of the heat-treated analogue also showed a broad hump, but with several sharp peaks that were indexed and found to correspond with the trevorite diffraction pattern (Fig. 1 right). Trevorite crystallization was quantified using a CaF_2 intensity standard and was found to be 24 wt% in the glass. Importantly, since crystals can settle during heat treatment it is difficult to obtain a monolithic XRD sample with a composition that is representative of the entire glass. Thus, there is some inherent uncertainty in the crystal content from sample to sample; however, we attempted to avoid this uncertainty by obtaining samples that contained all portions of the glass puck (e.g. a cross-sectional piece containing, the top, bulk, and bottom of the glass). A photo of non-crystallized and trevorite-crystallized **A-G** is shown in Fig. 2. The non-crystallized analogue is black and shiny, which is typical of nuclear waste glass simulants due to the large number of metals present in the glass. Trevorite crystallization in the glass matrix causes the glass to possess a dull, brown-red color, with a ceramic texture.

When a 500 mg piece of non-crystallized **A-G** was irradiated inside our microwave cavity at 300 W, the glass immediately began to heat at approximately 1.3 °C/sec until reaching approximately 100 °C. Above 100 °C the heating occurred even slower, at a rate of approximately 0.25 °C/sec until reaching steady state at 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 thirty minutes, the glass temperature never exceeded 450 °C. Similar results were observed on multiple samples, although some variations in the extent of heating and heating rate were observed. 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 °C are shown as a function of the irradiation time in Fig. 3.

Since a truly amorphous glass should show minimal dielectric heating due to the lack of polarizability, the mechanism of heating for the amorphous glass is not known, but may occur from the dielectric loss of small ordered regions in the glass, referred to as clusters or quasicrystals, which have been reported elsewhere.[13] These clusters often have atomic arrangements that approach those of crystals however, they do not possess long-range ordering like crystalline solids.[26,27]

The microwave heating of a 500 mg monolith of the trevorite-crystallized analogue of **A-G** occurred faster and reached much higher temperatures than the non-crystallized version. Although there was some variation in the heating rate and maximum temperature, generally the samples heated at a rate of approximately 16 °C/sec from room temperature to approximately 400 °C. Above 400 °C the samples, on average, heated less rapidly at a rate of approximately 12 °C/sec. IR radiometry measurements showed that temperatures for these samples reach a plateau of approximately 1600 °C after only 2 minutes. Samples were not kept at temperatures near 1600 °C for long due to the potential for volatility that could result in alteration of the glass composition. Thus, partially crystalline samples heated roughly two orders of magnitude faster and reached much higher temperatures than non-crystalline samples. 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 caused by slight inhomogeneity. IR images of a typical irradiated piece of partially crystallized **A-G** are shown as a function of the irradiation time in Fig. 4.

After being irradiated for 2 minutes, these samples were cooled and visually inspected for physical changes. It was clear from inspection that microwave heating had melted the crystallized glass, and transformed it from dull and reddish brown to shiny and black, similar to the non-crystalline version of **A-G** as shown in Fig. 5. This result suggested that the crystalline components of **A-G** had been melted/dissolved during irradiation. Additionally, when previously melted samples were placed back inside the microwave cavity for further irradiation, the samples exhibited poor heating (Fig. 6) similar to the heating seen in non-crystalline **A-G**. XRD measurements of irradiated samples were absent of crystalline peaks, proving there was no detectable trevorite left in the glass matrix. It is therefore clear that rapid cooling of **A-G** below the glass transition temperature, kinetically prohibits the glass from reforming trevorite, thus explaining why re-irradiated samples of **A-G** exhibited poor heating.

To study the effects of microwave power on the heating rate in **A-G**, temperature measurements for non-crystalline and crystalline **A-G** were made while limiting microwave power to 50 W, 100 W, 200 W, and 300 W (Fig. 7). The heating rate of both samples is significantly lower under low microwave power and higher under high microwave power. While this result was expected, it highlights the microwave utility in terms of controlling the temperature of microwave specific heating sites.

Importantly, previous studies on microwave processing of simulated nuclear waste glasses and fusion of melter feed have employed microwave hybrid heating using external attenuators like silicon carbide to heat glass indirectly.[28,29] These attenuators interact strongly with microwave radiation then transfer heat from the attenuator to the surrounding glass environment. Therefore, the heating is not site-specific and would not be useful for selectively dissolving/melting crystals dispersed in a glass matrix, since the glass would exceed operational temperature limits and radionuclide volatilization could occur.

Conclusions

Microwave heating of partially crystallized HLW glass simulants was shown to be power-dependent and 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 high melting point crystals within a glass melter; a result that could help remediate the negative and potentially costly effects of crystal accumulation in a melter. Future investigations are planned to study the heating effects for glass with varying crystal content and crystal composition, which should provide information on the ability to heat various crystals at a low ratio in a glass melt. Also, future work is needed to determine whether localized volatilization of glass and radionuclides occurs in close proximity to microwave heated crystals, and whether these volatiles can be quenched as they travel through a cooler glass melt.

Acknowledgements

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References

1. A. C. Metexas and R. J. Meredith, “Industrial Microwave Heating,” IET: Power and Energy Series, **4** (1983).

2. S. Kumar and S. Shukla, “Concepts and Applications of Microwave Engineering,” PHI Learning Private Limited: Delhi, India (2014).

3. D. Stuerga, “Microwave Athermal Effects in Chemistry: A Myth's Autopsy. Part I: Historical Background and Fundamentals of Wave-Matter Interaction,” *J. Microw. Power Electromagn. Energy*, **31** 87-100 (1996).

4. D. Stuerga, “Microwave Athermal Effects in Chemistry: A Myth's Autopsy. Part II: Orienting Effects and Thermodynamic Consequences of Electric Field,” *J. Microw. Power Electromagn. Energy*, **31** 101-113 (1996).

5. M. R. Rosana, J. Hunt, A. Ferrari, T. A. Southworth, and Y. Tao *et al*, “Microwave-Specific Acceleration of a Friedel–Crafts Reaction: Evidence for Selective Heating in Homogeneous Solution,” *The Journal of Organic Chemistry*, **79** 7437-7450 (2014).

6. P. Lidström, J. Tierney, B. Wathey, and J. Westman, “Microwave Assisted Organic Synthesis—A Review,” *Tetrahedron*, **57** 9225-9283 (2001).

7. Y.-J. Zhu and F. Chen, “Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase,” *Chemical Reviews*, **114** 6462-6555 (2014).

8. D. F. Bickford and C. M. Jantzen, “Devitrification of SRL Defense Waste Glass,” *Sci. Basis for Nuclear Waste Management VII, G.L McVay (ed). Elsevier Publ., New York*, 557-565 (1984).

9. C. M. Jantzen, K. G. Brown, and J. B. Pickett, “Durable Glass for Thousands of Years,” *Int. J. Appl. Glass Sci*, **1** 38-65 (2010).

10. J. D. Vienna, “Nuclear Waste Vitrification in the United States: Recent Developments and Future Options,” *Int. J. Appl. Glass Sci*, **1** 309-321 (2010).

11. C. R. MacFrarlane and M. Fragoulis, “Theory of Devitrification in Multicomponent Glass Forming Systems Under Diffusion Control,” *Physics and Chemistry of Glasses*, **27** 228-234 (1986).

12. Shelby, J. E., “*Introduction to Glass Science and Technology*,” The Royal Society of Chemistry, (1997).

13. D. F. Bickford and C. M. Jantzen, “Devitrification of Defense Nuclear Waste Glasses: Role of Melt Insoluble,” *J. Non-Cryst. Solids*, **84** *299-307* (1986).

14. C. M. Jantzen and K. G. Brown, “Predicting the Spinel-Nepheline Liquidus for Application to Nuclear Waste Glass Processing. Part I: Primary Phase Analysis, Liquidus Measurment, and Quasicrystalline Approach,” *J. Am. Ceram. Soc.*, **90** 1866-1879 (2007)

15. M. J. Plodinec and J. R. Wiley, “Viscosity and Electrical Conductivity of Glass Melts as a Function of Waste Composition,” *Proceedings International Symposium on Ceramics in Nuclear Waste Management CONF-790420 Edited by T. D. Chickalla, and J. E. Mendel. U. S. DOE, Cincinnati, OH*, 210 (1979).

16. A. K. Varshneya, “Fundamentals of Inorganic Glasses,” Harcourt Brace & Company: (1994).

17. J. E. Till and H. A. Grogan, “Radiological Risk Assessment and Environmental Analysis,” Oxford University Press, Inc.: New York, New York (2008).

18. C. M. Jantzen, and K. G. Brown, “Predicting the Spinel-Nepheline Liquidus for Application to Nuclear Waste Glass Processing. Part II: Quasicrystalline Freezing Point Depression Model,” *J. Am. Ceram. Soc.,* **9**, 1880-1891 (2007).

19. R. A. Robie, B. S. Hemingway, and J. R. Fisher, "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures," U.S. Geological Survey Bulletin (1979).

20. D.-S. Kim, and J. D. Vienna, "Influence of Glass Property Restrictions on Hanford Glass Volume" *Ceram. Trans.: Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries VII*, **132** 105-115 (2002).

21. Materials Data Incorporated. *http://www.materialsdata.com/about.htm*.

22. PDF-4+ by International Center for Diffraction Data. *http://www.icdd.com/products/pdf4.htm*.

23. J. G. P. Binner, B. Vaidhyanathan, and J. Wang, "A Comparative Study of Temperature Measurements During Microwave Processing," *Proceedings of the 9th International Conference on Microwave and High Frequency Heating*, Loughborough, U.K., Loughborough, U.K., 477-480 (2003).

24. G. B. Dudley, R. Richert, and A. E. Stiegman, "On the Existence of and Mechanism for Microwave-Specific Reaction Rate Enhancement," *Chemical Science*, **6** 2144-2152 (2015).

25. A. Kouchakzadeh, "Microwave Pentration Depth in Bulk Pistachios," *Int. J. Emerg. Sci.* **3** 303-310 (2013).

26. G. E. Brown Jr., F. Farges, and G. Calas, "X-Ray Scattering and X-Ray Spectroscopy Studies of Silicate Melts," Mineralogic Society of America: Washington, DC, **Vol. 32** (1995).

27. W. Burnham, "The Nature of Multicomponent Aluminosilicate Melts," *Phys. Chem. Earth*, **13 and 14** 191-227 (1981).

28. R. L. Schulz, Z. Fathi, D. E. Clark, and G. G. Wicks, “Microwave Processing of Simulated Nuclear Waste Glass,” *Ceram. Trans: Nuclear Waste Management IV*, 779-786 (1991).

29. C. M. Jantzen, J. R. Cadieux, “Characterization of Radioactive Waste Melter Feed Vitrified By Microwave Energy,” *Ceram. Trans: Nuclear Waste Management IV*, 743-751 (1991)

Figure Caption List:

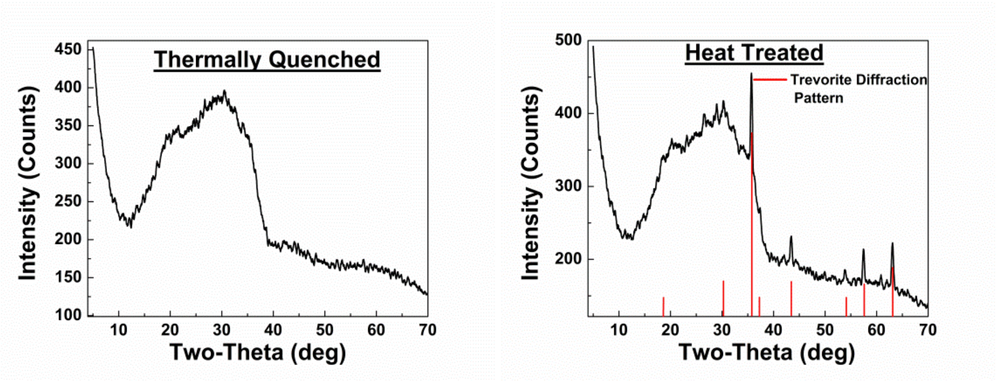

Fig. 1. X-ray Diffraction patterns of **A-G** formed by rapid thermal quenching on a stainless steel plate (left) and a 24 hr. heat treatment at 850 °C (right). Quenched samples exhibit a broad hump that is characteristic of amorphous glass. Heat treated samples shows a similar hump but with sharp diffraction peaks that are characteristic of trevorite ($NiFe_2O_4$).

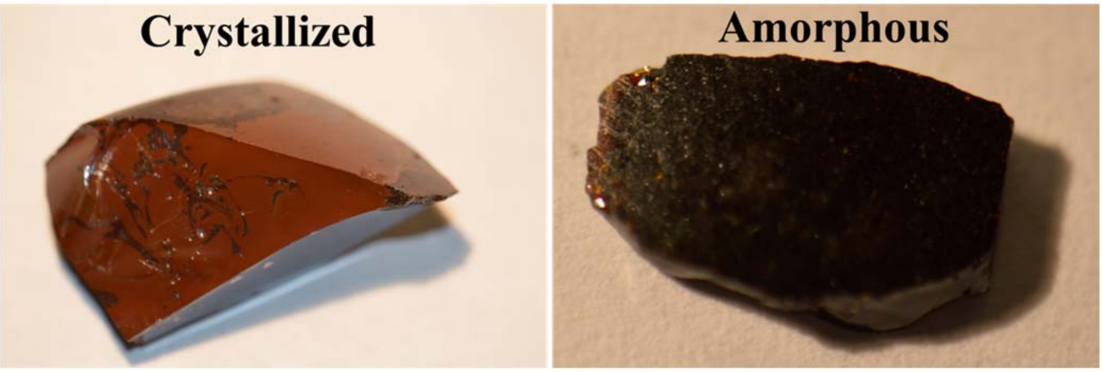

Fig. 2. Photo of partially crystallized (left) and non-crystallized (right) monoliths of **A-G**. As can be seen, the non-crystallized analogue is black and shiny while the partially crystallized analogue is brown-red and dull.

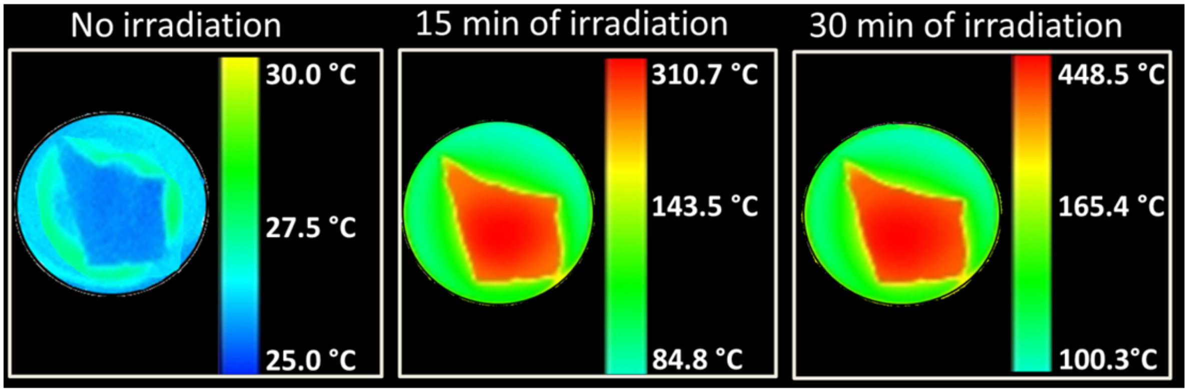

Fig. 3. IR radiometry images of non-crystalline **A-G** under microwave irradiation for increasing amounts of time. The glass is the shapeless object at the center of the circular image. The temperature of the glass ultimately plateaus around 450 °C.

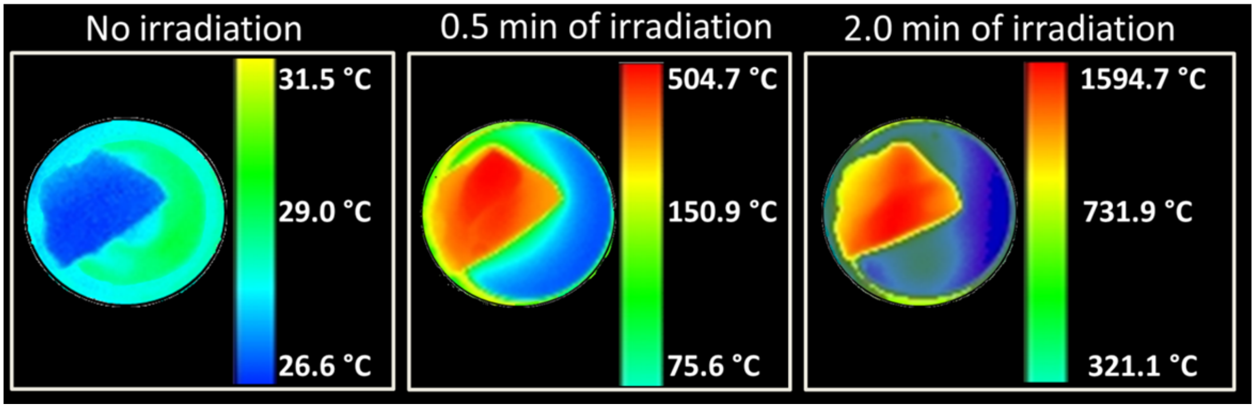

Fig. 4. IR radiometry images of a partially crystallized piece of **A-G** under microwave irradiation for varying amounts of time. The glass is the shapeless object at the center of the circular image. The glass can be seen melting and changing shape at 2 minutes as the temperature rises above 1000 °C.

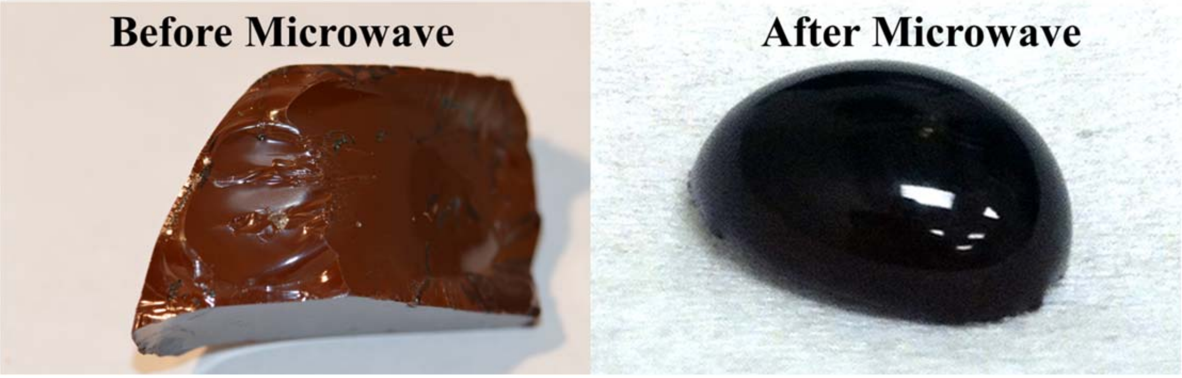

Fig. 5. Photographs of partially crystallized **A-G** before (left) and after (right) 2 minutes of microwave irradiation.

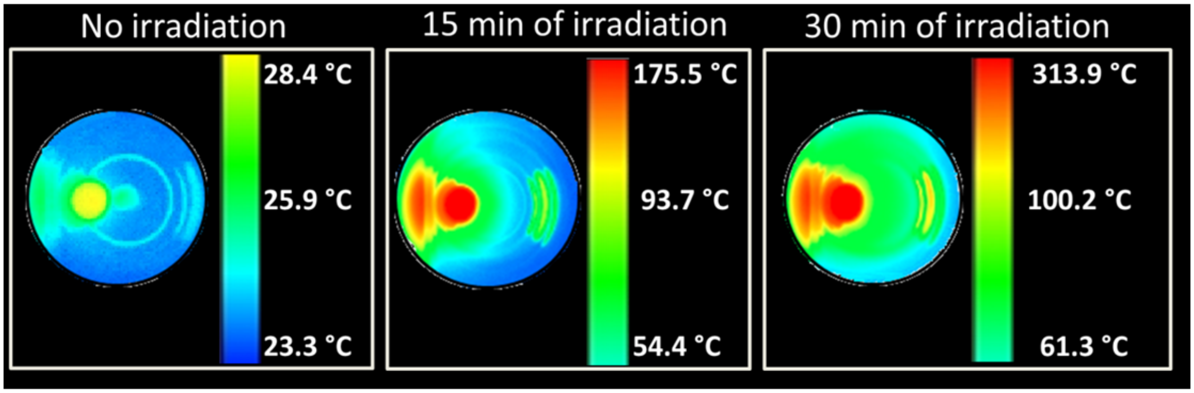

Fig. 6. IR radiometry images of a previously irradiated and melted piece of **A-G** under microwave irradiation for varying amounts of time. The glass is the circular object near the center of the circular image. This glass exhibits poor microwave heating due to the lack of a trevorite phase.

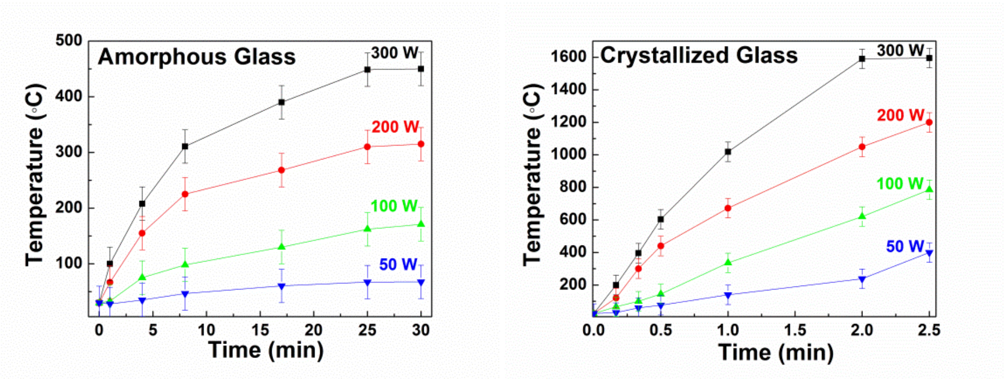

Fig. 7. (left) The temperature of non-crystalline **A-G** and (right) crystallized **A-G** is displayed as a function of microwave irradiation time at different microwave powers. Error bars were generated based on the temperature variations observed in multiple measurements.

Table 1. Target Composition of **A-G** 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
NaF	0.02
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