

Project No. 15-8081

# Understanding Influence of Thermal History and Glass Chemistry on Kinetics of Phase Separation and Crystallization in Borosilicate Glass-Ceramic Waste Forms for Aqueous Reprocessed High Level Waste

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Fuel Cycle Research and Development

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**Final Scientific/Technical Report**  
For deposit in OSTI

**Project Title:**

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**Report Number:** DOE-WSU-8431-1

**Date of Report:** December 17, 2018

**Period of Performance:** October 1, 2015 – September 30, 2018

**Award Number:** NU-15-WA-WSU-0203-02 (DE-NE0008431)

**Project Number:** 15-8081

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## Acronyms and Abbreviations

ACERS	American Ceramic Society
ANL	Argonne National Laboratory
APS	Advanced Photon Source
BL	Beamline
DOE	Department of Energy
DTA	Differential thermal analysis
EDS	Energy Dispersive Spectroscopy
EPMA	Electron Probe Microanalysis
EPR	Electron Paramagnetic Resonance
EPSRC	Engineering and Physical Sciences Research Council
EXAFS	Extended X-ray Absorption Fine Structure
GOMD	Glass and Optical Materials Division
HLW	High-level waste
HFIR	High Flux Isotope Reactor
MRS	Materials Research Society
MS&T	Materials Science & Technology
ND	Neutron Diffraction
NEUP	Nuclear Energy University Program
NMR	Nuclear Magnetic Resonance
NOMAD	Nanoscaled Ordered Materials Advanced Diffractometer
ORNL	Oak Ridge National Laboratory
PI	Principal Investigator
PNNL	Pacific Northwest National Laboratory
RE	Rare earth
SANS	Small-Angle Neutron Scattering
SAXS	Small-Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SGT	Society for Glass Technology
SNS	Spallation Neutron Source
TEM	Transmission Electron Microscopy
WSU	Washington State University
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

# 1 REPORT SUMMARY

This report provides an overview of the research activities conducted over the three-year period, October 1, 2015 to September 30, 2018. The project consisted of the US DOE component and a parallel project funded by the UK's EPSRC. The US project is reported here, with some overview of the UK project results. The project was designed to be highly collaborative, including work in the US by Washington State University and Rutgers University, and in the UK by the University of Sheffield and the University of Warwick. Pacific Northwest National Laboratory supported the US project with some synthesis and some characterization. The overall program had two aims: (Aim 1) Understand fundamental mechanisms of the phase transitions leading to the conversion of melt to multiphase glass-ceramic as a function of composition and cooling rate; (Aim 2) Understand influence of glass chemistry on kinetics of phase separation and crystallization. This report includes the summary of the project objectives, approaches, results and deliverables.

## 1.1 Scientific Accomplishments

### Aim 1: Fundamental mechanisms of phase transitions leading from melt to glass-ceramic

- Obtained temperature dependent phase composition and microstructure using hold and quench experiments, with samples characterized by TEM, SEM, SAXS, XRD, Na-23 NMR
- Studied cooling rate and container dependence of total crystal fraction
- Obtained activation energies for crystallization of oxyapatite in selected compositions
- Developed methods for in-situ neutron and X-ray experiments to investigate crystallization on cooling from melt

### Aim 2: Influence of glass chemistry on phase separation and crystallization

- Synthesized and studied glasses from 23 variation series, constituting a total of ~80 glass compositions
- Investigated single component effects including Na, Ca, Mo, RE, Zr, Ti, Ru
- Investigated importance of ratios including B/RE, Na/B
- Investigated glass structure in presence/absence of Mo as a function of RE concentration
- Investigated RE cation identity effects for glasses containing single RE oxides: La, Ce, Nd, Sm, Dy, Ho, Er, Tm, Yb, Lu, Y, or Sc
- Investigated the effect of RE cation size (Sc, Y, La, Lu) and paramagnetism (Er, Nd, Yb, Sm) on B-11 NMR signal
- Discovered that RE cation size plays a large role in crystal phase identity, particularly in peraluminous glasses with higher concentrations of RE oxide
- Discovered that rare earth cations partition into all major phases, including transition metal phases (powellite, zirconia), silicate phases (oxyapatite, keiviite), borosilicate phases (lanthanide borosilicate), and borate phases (lanthanide borate)

## 1.2 Ongoing and Future Activities

- Completion of study of rare earth size effect of peraluminous glasses and manuscript writing

- Editing and publication of manuscripts describing studies of La+Ce, La/Nd, and La/Er glass-ceramic series, including optical absorption and luminescence studies
- Publication of glass studies involving the effects of Zr and Ru oxides
- Publication of glass studies performed in the UK, including NMR studies
- In situ aerodynamic levitation experiment at the Advanced Photon Source at ANL
- Si-29 NMR on single phase RE oxyapatites

### 1.3 Publications

1. J. McCloy and A. Goel, "Glass-Ceramics for Nuclear Waste Immobilization," *MRS Bulletin*, 42(3), 233-240 (2017). <http://dx.doi.org/10.1557/mrs.2017.8>
2. Antoine Bréhault, Deepak Patil, Randall Youngman, Lynn Thirion, John Mauro, Claire Corkhill, John McCloy, Ashutosh Goel, "Compositional dependence of solubility/retention of molybdenum oxides in aluminoborosilicate based model nuclear waste glasses," *Journal of Physical Chemistry B*, 122(5), 1714-1729 (2018), <http://dx.doi.org/10.1021/acs.jpcc.7b09158>
3. D. S. Patil, M. Konale, M. Gabel, O.K. Neill, J.V. Crum, A. Goel, M.C. Stennett, N.C. Hyatt, and J.S. McCloy, "Impact of rare earth ion size on the phase evolution of MoO<sub>3</sub>-containing aluminoborosilicate glass-ceramics," *Journal of Nuclear Materials*, 510, 539-550, (2018). <https://doi.org/10.1016/j.jnucmat.2018.08.004>
4. John S. McCloy, Brian Riley, Jarrod Crum, José Marcial, Joelle Reiser, Karen Kruska, Jacob Peterson, Daniel Neuville, Deepak Patil, Kristian Barnsley, John V. Hanna, "Crystallization Study of Rare Earth and Molybdenum Containing Nuclear Waste Glass Ceramics," *Journal of the Ceramic Society*, submitted 10/26/18.
5. John McCloy, José Marcial, Brian Riley, Jorg Neufeind, Jarrod Crum, Deepak Patil, "Method Development for High Temperature In-Situ Neutron Diffraction Measurements of Glass Crystallization on Cooling from Melt," *MRS Advances*, submitted 11/14/18
6. John McCloy, Jose Marcial, Deepak Patil, Muad Saleh, Mostafa Ahmadzadeh, Hua Chen, Jarrod Crum, Brian Riley, Hrishikesh Kamat, Antoine Bréhault, Ashutosh Goel, Kristian Barnsley, John V. Hanna, Prashant Rajbhadari, Claire Corkhill, Russell Hand, Neil Hyatt, "Glass structure and crystallization in boro-alumino-silicate glasses containing rare earth and transition metal cations," *MRS Advances*, submitted 12/10/18.

### 1.4 Presentations

1. McCloy, "In-situ Crystallization Experiments of Nuclear Waste Glass Ceramics," SGT Centenary Conference, Sheffield, UK, September 2016.
2. McCloy, "Glass-ceramics for nuclear waste management," *Invited MRS Webinar*, March 22, 2017. <http://www.prolibraries.com/mrs/?select=session&sessionID=6308>
3. Bréhault "Compositional dependence of molybdenum solubility/retention in aluminoborosilicate glasses/glass-ceramics," MRS Fall meeting, Boston, November 2016.
4. Rajbhadari, "Formulation and Characterization of Improved High Level Waste Glass-Ceramic," MRS Fall meeting, Boston, November 2016.

5. Patil, "Effect of Rare Earths on the solubility and crystallization of Mo in borosilicate glasses for nuclear waste immobilization," Pacific Rim ceramic conference (PACRIM), Waikoloa, HI, May 24, 2017.
6. Goel, "Compositional Dependence of MoO<sub>3</sub> solubility in aluminoborosilicate Glasses," Pacific Rim ceramic conference (PACRIM), Waikoloa, HI, May 24, 2017.
7. Kamat, "Compositional Dependence of Crystallization in MoO<sub>3</sub> containing Aluminoborosilicate Glasses," ACERS GOMD, San Antonio, TX, May 2018.
8. Saleh, "Optical Characterization of Rare Earths Mo Containing Borosilicate Glasses and Glass Ceramics," ACERS GOMD, San Antonio, TX, May 24, 2018.
9. McCloy, "Crystallization of Rare-Earth Containing Phases in Molybdenum-Containing Alumino-boro-silicate Glasses," *Invited* presentation at MS&T18, Columbus, OH, October 15, 2018
10. McCloy, "Method Development for High Temperature In-Situ Neutron Diffraction Measurements of Glass Crystallization on Cooling from Melt," MRS Fall meeting, Boston, November 2018.
11. McCloy, "Glass structure and crystallization in boro-alumino-silicate glasses containing rare earth and transition metal cations," MRS Fall meeting, Boston, November 2018.
12. Chen, "Rare-earth containing crystalline phases in nuclear waste glass-ceramics: role of rare earth ion size," MRS Fall meeting, Boston, November 2018.

## 1.5 Programmatic accomplishments

As part of the program, three neutron beamtime sessions were completed, as well as three x-ray beamtime sessions

- ORNL SNS #IPTS-15446.1: "SANS and ND for Phase Evolution on Cooling of Nuclear Waste Glass Ceramic Melts," 2016. [2 sessions, one at HFIR GP-SANS and one at NOMAD for ND]
- ORNL SNS #IPTS-17308: "In situ high temperature glass ceramic experiment development (proof of concept)," BL-1B NOMAD, 2017.
- ANL APS, BL 9-ID-C, SAXS, USAXS, WAXS measurements, 2017.
- Photon factory synchrotron facility (Tsukuba, Japan), PF ring BL-27, Proposal #2017G187 Mo K-edge XAS, 2018.
- ANL APS GUP-54910, "Crystallization mechanism of glasses on cooling from melt of glasses from high temperature," BL 6-ID-D, 2018.

## 2 PROJECT BACKGROUND

A glass-ceramic waste form is being developed through the Department of Energy – Office of Nuclear Energy to immobilize non-fissionable waste streams of alkali (A, <sup>137</sup>Cs), alkaline-earths (AE, <sup>90</sup>Sr), rare earth (RE), and transition metals generated by the projected transuranic extraction (TRUEX<sup>plus</sup>) aqueous reprocessing of used nuclear fuel. Compared to an alkali borosilicate glass waste form, the glass-ceramic form is expected to double waste loading (to ~45%) and have

improved thermal stability. These benefits are realized by the partitioning of the insoluble fission product fraction into a suite of crystalline structures through controlled crystallization on cooling from the melt. The target phase assemblage is a glassy borosilicate matrix with crystalline  $\text{AEMoO}_4$  (powellite),  $(\text{RE,A,AE})_{10}\text{Si}_6\text{O}_{26}$  (oxyapatite),  $(\text{Ce,Zr,Ln})\text{O}_2$  (zirconia), and  $\text{RE}_5\text{BSi}_2\text{O}_{13}$  (rare earth borosilicate).

Fundamental mechanistic understanding of thermodynamic phase transitions and crystallization mechanisms occurring during synthesis of this glass-ceramic (as a function of thermal history and glass chemistry) is of paramount importance for international waste management programs, which seek to exploit glass-ceramic technology or, conversely, optimize conventional borosilicate glasses to improve the solubility of key fission products. This approach is also of critical importance in the UK scenarios, where glass-ceramics offer key advantages for post-operative clean out of Mo-rich residues from HLW storage tanks, disposition of plutonium residues, and efficient waste immobilization for advanced fuel cycles, to meet the aims of the UK Nuclear Industry Strategy.

Major outcomes of this effort included: training of graduate students in glass ceramic engineering of nuclear waste forms; highly relevant publications in peer-reviewed journals; and formal technical exchange between US and UK researchers. Nuclear waste management is a long-term problem involving a worldwide technical community, and these projects solidify international cooperation towards joint technical goals. Consequently, this program is a joint collaborative enterprise between leading researchers from the US and UK who, collectively, bring mutually complementary and compatible skills, capabilities, and interests required to achieve a paradigm shift in technical understanding of crystallization in glass ceramics for radioactive waste immobilization. The US portion of the research was funded by the Department of Energy Office of Nuclear Energy NEUP program, and the UK portion was funded by Engineering and Physical Sciences Research Council, Research Councils UK Energy Programme.

## 2.1 Project goals and objectives

The report presents an overview of the work accomplished in the framework of the US – UK collaborative research project aimed at understanding the

- (1) fundamental mechanisms of the *phase transitions* leading to the conversion of melt to a multiphase glass ceramic as a function of composition and cooling rate; and
- (2) influence of *glass chemistry* on kinetics of phase separation and crystallization.

## 2.2 Approach

The project aimed to advance our understanding about the fundamental science on the kinetics and mechanisms of liquid-liquid phase separation and crystallization of complex multiphase glass ceramics for immobilization of mixed alkali/alkaline earth, rare earth, and transition metal waste streams. The above objectives were realized through the performance of three inter-related tasks:

- (i) Understanding kinetics of phase separation and crystallization in baseline glasses,
- (ii) Influence of glass chemistry on phase transitions and chemical durability, and

**(iii)** *In-situ* high-temperature studies.

Overall, Task (ii) consisted of the majority of the effort, and over 80 glass compositions in over 20 carefully considered compositional series were synthesized, crystallized, and characterized with at least some of the following methods: visual investigation, scanning electron microscopy (SEM), SEM with energy dispersive spectroscopy (EDS), electron probe microanalysis (EPMA) using wavelength dispersive spectroscopy (WDS), X-ray diffraction (XRD), magic angle spinning – nuclear magnetic resonance (MAS NMR), X-ray absorption (XAS) [including X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS)], X-ray photoelectron spectroscopy (XPS), differential thermal analysis (DTA), Raman spectroscopy, optical absorption, and combined excitation-emission spectroscopy (CEES) [including photoluminescence (PL) and photoluminescence excitation (PLE)]. Chemical durability testing was not the focus of the effort, but a few experiments were performed on some UK glasses.

Surprisingly, Task (iii) presented considerably more technical difficulties than anticipated. Several neutron beamline experiments were needed to establish the parameterization for a reasonable *in-situ* neutron diffraction experiment. *In-situ* SANS experiments were unsuccessful. Ultimately, it was determined that *in-situ* high energy X-ray experiments will likely be more successful, and these experiments are currently scheduled but occur outside the contract period.

Task (i) is the understanding which is ultimately desired, and it depends on successful integration of the efforts in Tasks (ii) and (iii). In the proposal, Task (i) consisted of *study of the microstructure and chemical partitioning*, using electron microscopy, vibrational spectroscopy, diffraction, and NMR, as well as *in situ thermal analysis*, accomplished by hot-stage XRD, thermal analysis by DTA, and viscosity. The majority of effort was in studying the microstructure and chemical partitioning and a few experiments were done which could be considered *in-situ* thermal analysis.

### 3 SUMMARY AND CONCLUSIONS

#### 3.1 Understanding kinetics of phase separation and crystallization in baseline glasses

- It is clear that the precipitation of RE containing oxyapatite phases causes the drop in solubility of Mo in glass, further precipitating Mo droplets which convert to powellite.
- Some studies suggest that oxyapatite is the liquidus crystalline phase, but this is far from clear, and robust *in-situ* experiments are still needed to clarify this. This problem is exacerbated by the fact that the Mo-rich droplets may partition first, and they cannot easily be seen by diffraction since they remain amorphous or poorly crystalline until further cooled.
- The phase separation seen in the simplified 8-oxide system is different from that of the centroid glass composition, in that for the same heat treatment, the droplets are smaller and there is no initial Cs-rich phase separation.
- For the 8-oxide simplified peralkaline glass, 1250°C appears to be the critical temperature, below which isothermal holds then quench results in Mo droplet phase separation as well as oxyapatite and powellite crystallization.



- Viscosity measurements at high temperature as a function of spindle shear do appear to be able to detect liquid-liquid phase separation and/or crystallization.

### 3.2 Influence of glass chemistry on phase transitions

- Most peralkaline systems, defined as Na<sub>2</sub>O relative to Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub> by mole, appear to simply have powellite (if MoO<sub>3</sub> is present) and oxyapatite (if RE<sub>2</sub>O<sub>3</sub> is present)
- TiO<sub>2</sub> additions appear to drive molybdates crystallization from Na molybdate to powellite by requiring Na<sup>+</sup> cations to charge compensate TiO<sub>x</sub> polyhedra in the glass.
- Small RE cations result in keiviite precipitation rather than oxyapatite.
- Peraluminous systems are more complex, forming crystalline silicates (oxyapatite or keiviite), RE borates, or RE borosilicates, depending on the size of the RE cation.
- Peraluminous systems always crystallize a ZrO<sub>2</sub>-containing phase, as there is not enough Na<sub>2</sub>O to solubilize the Zr by charge compensating ZrO<sub>6</sub><sup>2-</sup> units.
- Adding small amounts of ZrO<sub>2</sub> or RuO<sub>2</sub> to the composition appears to have little effect for peralkaline glasses.
- RE oxides appear to affect the boron network, as smaller sized RE result in different more BO<sub>3</sub> as opposed to BO<sub>4</sub> units for the same mole fraction.
- As more RE oxides of a given type are added, more BO<sub>3</sub> relative to BO<sub>4</sub> units are created, at least for peralkaline glasses.

### 3.3 *In-situ* high-temperature studies.

- High temperature neutron experiments are difficult for glasses with volatile components like MoO<sub>3</sub>. Container choice is important, and influences crystal nucleation as well as ability to observe diffraction.
- Small angle experiments may be useful. Ex-situ SAXS on variously quenched samples gave some indication of phase separation, but data analysis was difficult and somewhat ambiguous.
- High temperature X-ray experiments are in progress, but volatilization will still be a problem for aerodynamic levitation experiments with melts above 1200°C. Specific cooling rates are difficult to achieve in these experiments.

## 4 RECOMMENDATIONS FOR FUTURE WORK

- A large number of glass compositions were tested during this program. As the results are written up and published, it would be a good idea to compile in one database all the compositions and key properties determined. This database could serve as a resource in the future for formulation and for understanding property-composition modeling.
- Once structure of glasses is compiled, more chemical durability measurements should be obtained for more selected glasses.
- In-situ crystallization techniques need more work. Several suggestions from the technical community have been made recently, including high-energy x-rays through Pt containers and anomalous small angle X-ray scattering (ASAXS). These first-of-a-kind measurements are time-consuming and complicated for complex glasses so take more time and effort than was possible on this current project.