Crystalline Ceramic Waste Forms: Reference Formulation Report

Fuel Cycle Research & Development

Prepared for

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Separations and Waste Forms

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SUMMARY

The research conducted in this work package is aimed at taking advantage of the long term thermodynamic stability of crystalline ceramics to create more durable waste forms (as compared to high level waste glass) in order to reduce the reliance on engineered and natural barrier systems. Durable ceramic waste forms that incorporate a wide range of radionuclides have the potential to broaden the available disposal options and to lower the storage and disposal costs associated with advanced fuel cycles. Assemblages of several titanate phases have been successfully demonstrated to incorporate radioactive waste elements, and the multiphase nature of these materials allows them to accommodate variation in the waste composition. Recent work has shown that they can be successfully produced from a melting and crystallization process. The objective of this report is to explain the design of ceramic host systems culminating in a reference ceramic formulation for use in subsequent studies on process optimization and melt property data assessment in support of FY13 melter demonstration testing.

The waste stream used as the basis for the development and testing is a combination of the projected Cs/Sr separated stream, the Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) waste stream consisting of lanthanide fission products, the transition metal fission product waste stream resulting from the transuranic extraction (TRUEX) process, and a high molybdenum concentration with relatively low noble metal concentrations. In addition to the combined CS/LN/TM High Mo waste stream, variants without Mo and without Mo and Zr were also evaluated.

Based on the results of fabricating and characterizing several simulated ceramic waste forms, two reference ceramic waste form compositions are recommended in this report. The first composition targets the CS/LN/TM combined waste stream with and without Mo. The second composition targets with CS/LN/TM combined waste stream with Mo and Zr removed. Waste streams that contain Mo must be produced in reducing environments to avoid Cs-Mo oxide phase formation. Waste streams without Mo have the ability to be melt processed in air. A path forward for further optimizing the processing steps needed to form the targeted phase assemblages is outlined in this report. Processing modifications including melting in a reducing atmosphere, and controlled heat treatment schedules are anticipated to improve the targeted elemental partitioning.

CONTENTS

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TABLES

ABBREVIATIONS

AFCI	Advanced Fuel Cycle Initiative
CCIM	Cold Crucible Induction Melter
CS	Cesium/Strontium
DOE	Department of Energy
EDAX	Energy Dispersive Spectroscopy
FCR&D	Fuel Cycle Research and Development
HLW	High Level Waste
LANL	Los Alamos National Laboratory
LN	Lanthanides
NM	Noble Metals
PCT	Product Consistency Test
PUREX	Plutonium, Uranium, Extraction Processes
Redox	Reduction/Oxidation
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SYNROC	Titanium based ceramic substance that can incorporate nuclear waste
TALSPEAK	Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes
TEM	Transmission Electron Microscopy
TM	Transition Metals
TRUEX	Transuranic Extraction
XRD	X-ray Diffraction

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1.   INTRODUCTION

Efforts being conducted by the United States Department of Energy (DOE) under the Fuel Cycle Research and Development (FCR&D) program are aimed at making potential U.S. fuel cycle options more effective by the development of next generation waste management technologies.[1]   One envisioned fuel reprocessing technology would separate the fuel into several fractions, thus, partitioning the waste into groups with common chemistry. Ceramic (or crystalline) waste forms incorporate the radionuclides in the waste as part of the crystal structure.[2] As such, ceramic forms are tailored to create certain minerals (i.e. unique crystalline structures) that will host the radionuclides by binding them in their specific crystalline network. Tailoring of a ceramic waste form is based on the knowledge that there are many naturally produced minerals containing radioactive and non-radioactive species very similar to the radionuclides of concern in wastes from fuel reprocessing. The research conducted in this work package is aimed at taking advantage of the long term thermodynamic stability of crystalline ceramics to create more durable waste forms (as compared to high level waste (HLW) glass) in order to reduce the reliance on engineered and natural barrier systems. Durable ceramic waste forms that incorporate a wide range of radionuclides have the potential to broaden the available disposal options and to lower the storage and disposal costs associated with advanced fuel cycles.

Titanate ceramics have been thoroughly studied for use in immobilizing nuclear wastes (e.g., the SYNROC family) due to their natural resistance to leaching in water.[2, 3] Assemblages of several titanate phases have been successfully demonstrated to incorporate radioactive waste elements, and the multiphase nature of these materials allows them to accommodate variation in the waste composition.[4] While these materials are typically densified via hot isostatic pressing, recent work has shown that they can also be produced from a melt. For example, demonstrations have been completed using the Cold Crucible Induction Melter (CCIM) technology to produce several crystalline ceramic waste forms, including murataite-rich ceramics,[5] zirconolite/pyrochlore ceramics,[6] Synroc-C (zirconolite, hollandite, perovskite),[7] aluminotitanate ceramics, and zirconia.[8]   This production route is advantageous since melters are already in use for defense HLW vitrification in several countries, and melter technology greatly reduces the potential for airborne contamination as compared to powder handling operations associated with hot isostatic pressing.

The objective of this report is to explain the design of ceramic host systems including a synopsis of FY10[9], FY11[10] and current FY12 results culminating in reference ceramic compositions for several targeted waste streams. These reference ceramic compositions will form the basis of subsequent studies on process optimization and melt property data assessment in support of FY13 melter demonstration testing.

2.   DESIGN OF CERAMIC HOST SYSTEMS

2.1.   Projected Waste Stream Compositions

The waste streams that formed the basis for the development and testing completed to date are given in Table 2-1. The cesium, strontium and lanthanide (CS/LN) composition is the result of a combination of the Cs/Sr separated stream and the Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) waste stream consisting of lanthanide fission products. The cesium, strontium, lanthanide, transition metal (CS/LN/TM) streams are comprised of the Cs/Sr stream, the lanthanide stream, and the transition metal fission product waste stream resulting from the transuranic extraction (TRUEX) process. The CS/LN/TM High Mo waste stream variant has a high molybdenum concentration with relatively low noble metal concentrations. In addition to the combined CS/LN/TM High Mo waste stream, variants without Mo and without Mo and Zr were also evaluated.

Table 2-1. Projected Waste Stream Compositions (wt %) for Waste Form Development.

Oxide	CS/LN/TM High Mo	CS/LN/TM No Mo	CS/LN/TM No Mo, Zr
Ag_2O	0.40	0.43	0.43
BaO	7.83	8.47	8.47
Br	0.08	0.09	0.09
CdO	0.39	0.43	0.43
Ce_2O_3	11.01	11.91	11.91
Cs_2O	10.22	11.05	11.05
Eu_2O_3	0.61	0.66	0.66
Gd_2O_3	0.57	0.62	0.62
In_2O_3	0.01	0.01	0.01
La_2O_3	5.62	6.08	6.08
MoO_3	13.88	-	-
Nd_2O_3	18.56	20.07	20.07
PdO	0.06	5.73	5.73
Pm_2O_3	0.06	0.06	0.06
Pr_2O_3	5.14	5.56	5.56
Rb_2O	1.50	1.63	1.63
Rh_2O_3	0.28	1.21	1.21
RuO_2	0.70	6.20	6.20
Sb_2O_3	0.04	0.05	0.05
SeO_2	0.29	0.32	0.32
Sm_2O_3	3.82	4.13	4.13
SnO_2	0.25	0.27	0.27
SrO	3.49	3.77	3.77
Tb_2O_3	0.01	0.01	0.01
TeO_2	2.33	2.52	2.52
Y_2O_3	2.23	2.41	2.41
ZrO_2	10.60	3.33	-

2.2.   Calculation of Waste Form Compositions

Ceramic host systems for this study were selected based on the objectives of forming durable titanate phases, using a minimum of additives to form the desired phases (i.e., achieving high waste loadings), and the ability to be fabricated from a melt. Many of the elements in the waste stream are known to react with

select additives to form stable crystalline phases of the types perovskite, pyrochlore, hollandite, powellite, and zirconolite. Elements with a +3 valance such as the most prevalent lanthanide in the waste stream, Nd^{+3}, readily form ABO_3 perovskite and related pyrochlore structures with titanium resulting in $NdTiO_3$ and $Nd_2Ti_2O_7$ type phases, respectively.[11, 12] The Cs and Rb elements in the waste are known to partition to a hollandite structure with the formula of $(Ba_xCs_y)(M, Ti)_8O_{16}$ with $M=Al^{+3}$, Mn^{+3}, Fe^{+3}, Ga^{+3}, Cr^{+3}, Sc^{+3}, Mg^{+2} containing mixtures of divalent and trivalent cations.[13] FY12 single phase work from the FCRD program indicated that Fe and Al additions to the Cs containing hollandite improved phase formation when processed in air resulting in the targeted hollandite composition of $Ba_1Cs_{0.28}Al_{1.46}Fe_{0.82}Ti_{5.72}O_{16}$. These results complement previous SYNROC studies fabricating hollandite structures that involved waste streams from a plutonium, uranium, extraction processes (PUREX) which included Fe as a waste stream element.[14] Molybdenum in the waste stream has been shown to partition to an oxide based powellite phase,[10] or a metallic phase when processed under reducing conditions.[15] A $CaZrTi_2O_7$ zirconolite crystalline phase has been demonstrated to incorporate the Zr transition metal waste element.[16]

Based on single phase synthesis work in this project and a comprehensive literature review of crystalline ceramic waste forms, the additives Al_2O_3, BaO, CaO, TiO_2, and Fe_2O_3 were used to tailor waste forms based on the waste streams listed in Table 2-1. The choice of additives and targeted waste form compositions were calculated in a systematic fashion described below:

1) Select targeted phases for the specific waste stream. Options include:
   a. Powellite- $CaMoO_4$
   b. Zirconolite- $CaZrTi_2O_7$
   c. Perovskite- $NdTiO_3$
   d. Hollandite- $Ba_1Cs_{0.28}Al_{1.46}Fe_{0.82}Ti_{5.72}O_{16}$
2) Calculate the amount of additives necessary to form the targeted phase based on stoichiometry
   a. Powellite- From Mo content in waste stream, calculate CaO additions to form $CaMoO_4$
   b. Zirconolite-From Zr content in waste stream, calculate CaO and TiO_2 additions to form $CaZrTi_2O_7$
   c. Perovskite- From sum of M^{+3} elements in waste stream (Ce, Eu, Gd, La, Nd, Pr, Sm, Y), calculate TiO_2 additions to form $MTiO_3$
   d. Hollandite- From Cs, Rb and BaO content in the waste stream, calculate excess BaO, Al_2O_3, and TiO_2 additions to form $Ba_1Cs_{0.28}Al_{1.46}Fe_{0.82}Ti_{5.72}O_{16}$
3) Calculate waste form composition by dividing the amount of additive by the total amount of material required (waste stream + Al_2O_3, BaO, CaO, TiO_2, and Fe_2O_3 additives) X 100 for weight %
4) Additional compositions achieved by varying the amount of additives and waste loading from the compositions obtained in step 3 above.

   Note:

   i. Several low level elements in the waste stream were omitted due to low concentrations (Br, In_2O_3, Pm_2O_3, Sb_2O_3, and Tb_2O_3
   ii. Elements Cd, Se, Sb, Te were not accounted for in the targeted phase calculations.

Simulated waste material and the ceramic forming additives were blended in the appropriate ratios via ball milling. A majority of the samples were fabricated by melt processing in air. Select samples were melt processed under a reducing environment produced by flowing 100 ml/min of $1\%H_2$ balance Argon gas. A Pt/Rh alloy crucibles were used in air atmosphere, while high purity Al_2O_3 crucibles were used in reducing environments to prevent potential metal alloying and vessel degradation. Details of the

simulated waste, additives, and melting and crystalizing processes, and characterization are described in the FY10 and FY11 reports.[9, 10]

3. COMPOSITION SUMMARY

The following two sections describe the structure of waste forms fabricated by a melting and crystallizing process in air across a broad composition range. The microstructures of each sample are presented along with a table indicating the elemental composition and crystalline phases observed. A summary of the compositions studied in comparison with literature SYNROC values are presented at the end of the section in Table 3-5.

3.1. Combined Waste Forms *CS/LN/TM High Mo*

3.1.1. Al Rich- High Waste Loadings-CSLNTM-2

The sample CSLNTM-2 represents a composition rich in Al_2O_3 additive (14 wt %) and elevated waste loadings (60 wt %) Figure 3-1 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-1. Residual alumina was detected along with powellite, perovskite, zirconolite and a Cs-Mo phase, most likely a Cs_2MoO_4 analogue.

Figure 3-1. CS/LN/TM-2 Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph

Table 3-1. CSLNTM-2 Summary of Elements and Crystalline Phases (*Crystalline phases determined from XRD measurements and EDAX elemental analysis*)

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Al,	Al_2O_3
2	O, Mo, Ba, Nd	Powellite- $BaMoO_4$ doped + Cs_2MoO_4
3	O,Ti, Nd, Ce, Sm	Perovskite- $NdTiO_3$ Sm, Ce doped
4	O, Zr, Ti, Ca	Zirconolite- $CaZrTi_2O_7$

3.1.2. Ti Rich- High Waste Loadings-CSLNTM-10

The sample CSLNTM-10 represents a composition with TiO_2 rich additives (40 wt %) and high waste loadings (50 wt %). Figure 3-2 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-2. An Al doped Zirconia phase along with powellite, perovskite, and zirconolite were detected. A hollandite phase was not detected and relatively low Cs and Mo durability observed for this composition suggests the presence of a Cs-Mo phase similar to that observed with sample CSLNTM-2.
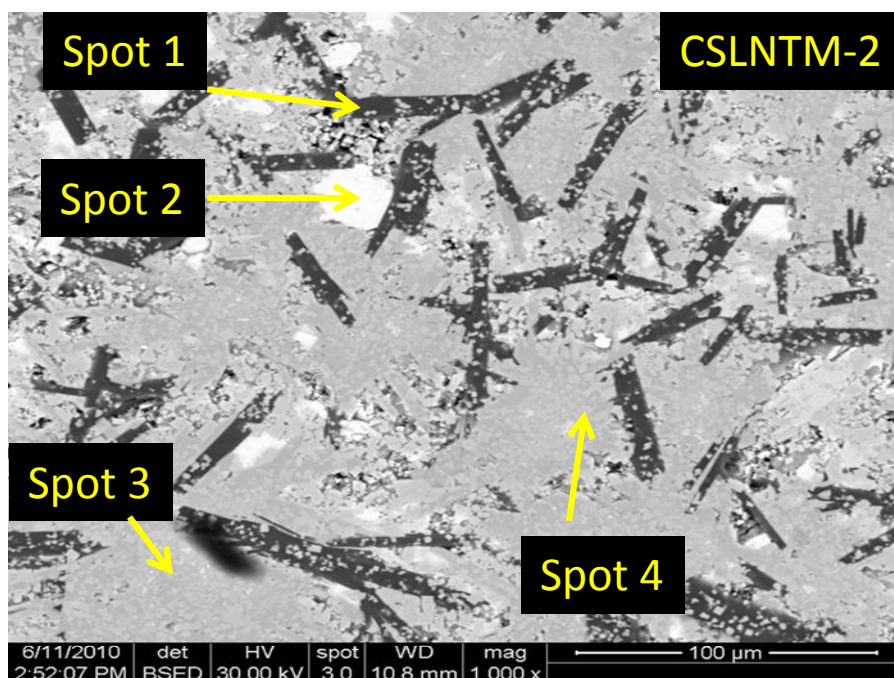

Figure 3-2. CSLNTM-10 Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph

Table 3-2. CSLNTM-10 Summary of Elements and Crystalline Phases *(*Crystalline phases determined from XRD measurements and EDAX elemental analysis)*

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Al, Zr	$Al_{0.1}Zr_{0.9}O_{1.95}$
2	O, Mo, Ba, Nd, Sr	Powellite- $BaMoO_4$ doped
3	O,Ti, Nd, Ce, Ca, Gd	Perovskite- $(CaNd)TiO_3$ Gd, Ce doped
4	O, Zr, Ti	Zirconolite- $CaZrTi_2O_7$

3.1.3.Ba + Fe Additions- Targeted Waste Loadings-CWAFH

Significant hollandite phase formation was not observed in the CSLNTM-2 and 10 compositions described above. The sample CWAFH represents a composition targeting hollandite formation through the addition of Ba and Fe oxide as additives. Figure 3-3 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-3. The targeted hollandite phase was observed along with powellite, perovskite, zirconolite, and Cs-Mo, Cs-Ti phases.

Figure 3-3. CWAFH Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph

Table 3-3. CWAFH Summary of Elements and Crystalline Phases *(*Crystalline phases determined from XRD measurements and EDAX elemental analysis)*

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Mo, Cs, Ti	Cs_2MoO_4 & Cs_2TiO_3
2	O, Ti, Al,Ba	Hollandite- $BaAlTi_5O_{14}$
3	O,Ti, Zr	Zirconolite- $CaZrTi_2O_7$
4	O,Ti, Zr	Zirconolite- $CaZrTi_2O_7$
5	O, Mo, Ba, Ca, Nd, Sr	Powellite- $BaMoO_4$ doped
6	O, Ti, Zr, Ca, Nd	Perovskite- $(CaNd)TiO_3$, $CaZrO_3$

3.1.4. Ca Rich, Ba + Fe Additions- Targeted Waste Loadings- CW-AFHZ+100Ca

The sample CWAFHZ+100 CaO represents a composition targeting hollandite (Ba and Fe oxide additions) and zirconolite (CaO) formation. Figure 3-4 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-4. The targeted hollandite and zirconolite phases were observed along with perovskite, powellite, and a Cs-Mo phase.

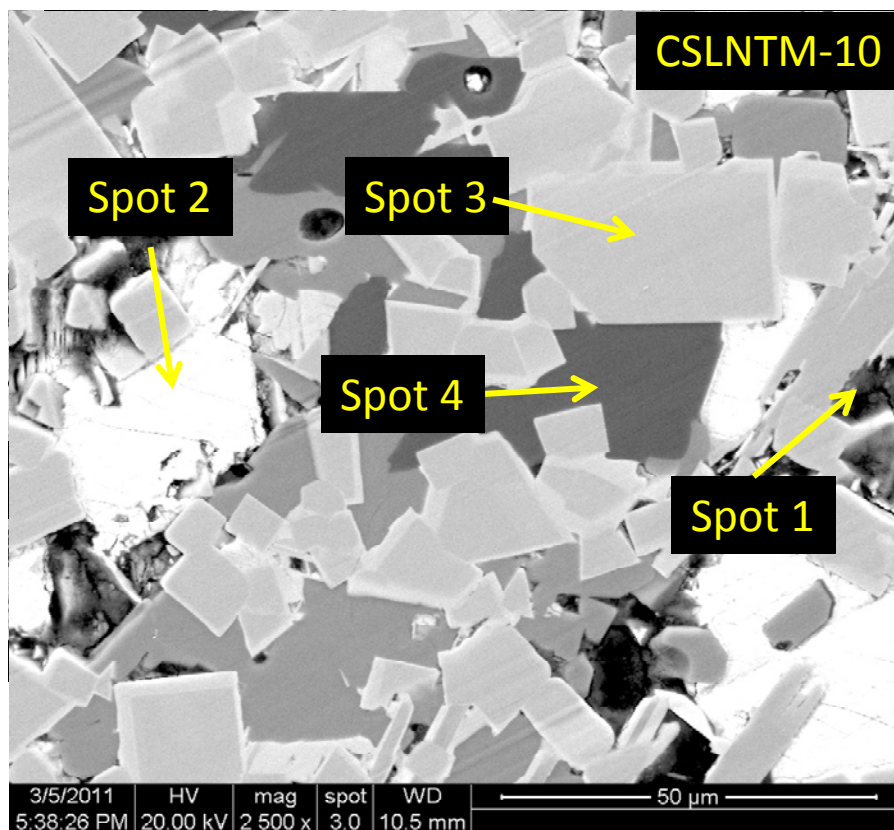**Figure 3-4. CWAFHZ+100 Ca Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph**

Table 3-4. CWAFHZ+100CaO Summary of Elements and Crystalline Phases *(*Crystalline phases determined from XRD measurements and EDAX elemental analysis)*

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Ti, Al, Ba, Fe	Hollandite- $BaAl_{1.46}Fe_{0.8}Ti_5O_{14}$
2	O, Ti, Ca, Nd, Gd, Fe	Perovskite-$CaTiO_3$
3	O, Mo, Cs, Ba, Ca, Sr, Nd	Cs_2MoO_4 + $(BaCa)MoO_4$
4	O,Ti, Zr, Nd, Gd	Zirconolite- $CaZrTi_2O_7$

Table 3-5 summarizes the broad range of compositions examined to incorporate CSLNTM High Mo waste streams. It was observed that additional Ba and Fe additions were essential to form the targeted Cs containing hollandite phase when melting and crystallizing in air. However, there was competition between Cs entering the hollandite phase and partitioning with Mo to form a low durability Cs-Mo phase. These phases have been observed in SYNROC processed in oxidizing environments and have exhibited low durability.[15]

Table 3-5. Ceramic Waste Form Compositions for CS/LN/TM High Mo Waste Stream.

Composition	CSLNTM-2	CSLNTM-10	CW-AFH	CW-AFHZ+100Ca	SYNROC-C*
Waste	60	50	27.8	25.8	19.81
Al_2O_3	14	3	6.58	6.09	4.63
TiO_2	21	40	46.88	46.94	61.4
CaO	5	7	1.51	5.29	9.59
BaO	-	-	11.36	10.52	4.57
Fe_2O_3	-	-	5.79	6.34	0.894

3.2. Waste Forms from Modified Waste Stream Elements

Cs-Mo phases were found to be present (XRD, EDAX and/or high Cs, Mo release rates in durability testing) across a broad composition range when processed from a melt and crystallization process in air. Due to the problems with Cs-Mo phase formation, several trials were performed with Mo and Mo plus Zr removed from the waste stream to evaluate the impact on phase formation.

3.2.1. Waste Forms from CS/LN/TM No Mo

The sample CWAFHZ-NoMo represents a composition targeting hollandite, perovskite, and zirconolite phase formation. Figure 3-5 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-6. The targeted hollandite, perovskite, and zirconolite phases were observed along with Cs-Ti and Cs-Te phases.
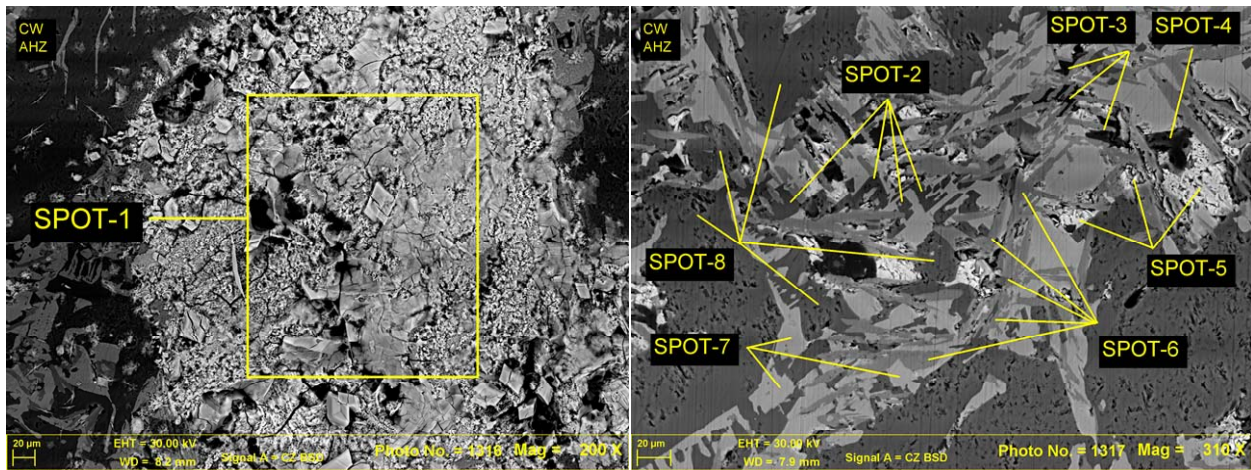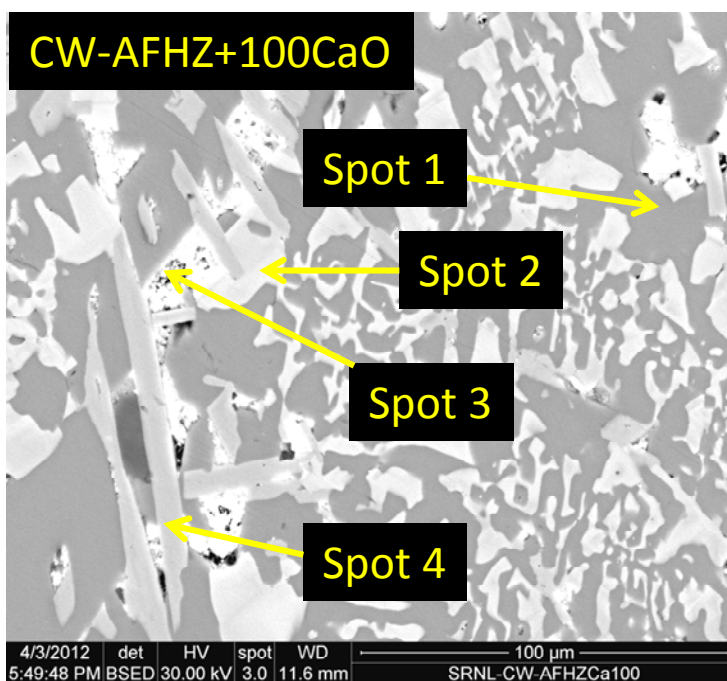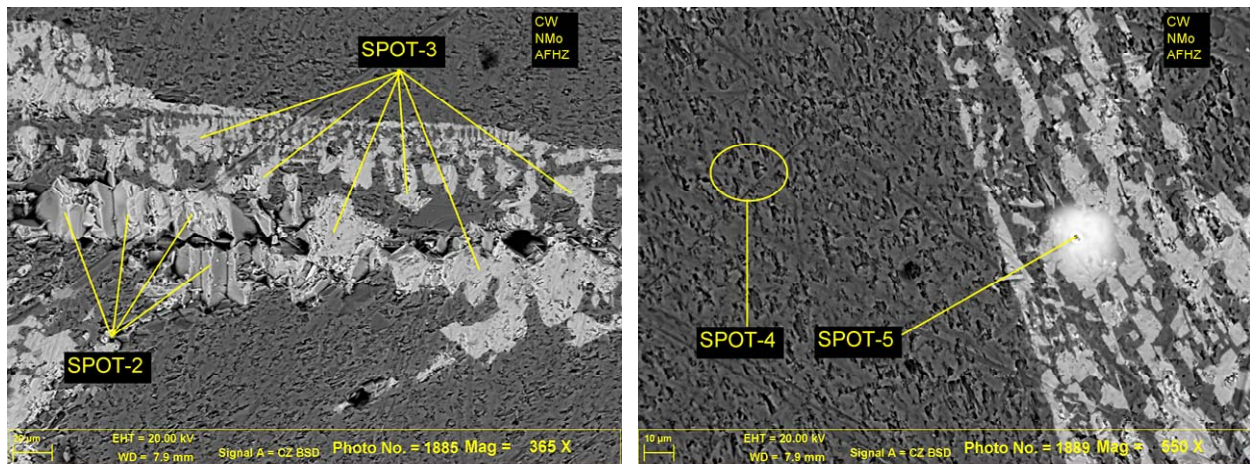

Figure 3-5.   CWAFHZ-NoMo Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph

Table 3-6. CWAFHZ-NoMo Summary of Elements and Crystalline Phases (**Crystalline phases determined from XRD measurements and EDAX elemental analysis*)

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Ti, Zr, Ca	Zirconolite-$CaZrTi_2O_7$
2	O, Ti, Nd, Ce, Ca	Perovskite- ($CaNdTiO_3$), Ce doped
3	O, Ti, Al, Ba,Fe	Hollandite- $BaAl_{1.46}Fe_{0.8}Ti_5O_{14}$
4	O, Cs, Ti, Te	Cs_2TeO_4, Cs_2TiO_3
5	O, Ti, Zr, Ca	Zirconolite-$CaZrTi_2O_7$

3.2.2. Waste Forms from CS/LN/TM No Mo, Zr

The sample CWAFHZ-NoMoZr represents a composition targeting hollandite and perovskite phase formation. Figure 3-6 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-7. The targeted hollandite and perovskite phases were observed along with Cs-Al-Ti, most likely non-durable $CsAlTiO_4$.
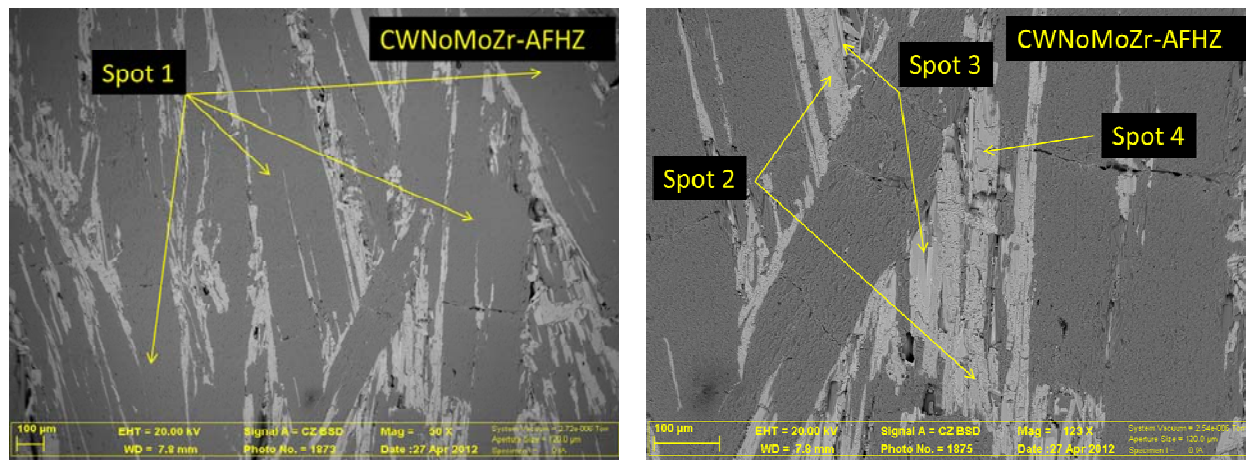
Figure 3-6.   CWAFHZ-NoMoZr Fabricated by Melting and Crystallizing in Air-Backscattered Electron Micrograph

Table 3-7. CWAFHZ-NoMoZr Summary of Elements and Crystalline Phases (**Crystalline phases determined from XRD measurements and EDAX elemental analysis*)

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Ti, Al, Ba, Fe	Hollandite- $BaAl_{1.46}Fe_{0.8}Ti_5O_{14}$
2	O, Ti, Nd,Ce	Perovskite- $NdTiO_3$
3	O,Ti, Ce,Y,Nd	Perovskite- $NdTiO_3$ Y, Ce doped
4	O,Ti, Cs,Nd,Al,P	$CsAlTiO_4$

3.3. Processing in a Reducing Environment

The phase formation of SYNROC materials is known to vary with processing conditions including oxidizing and reducing environments.[15] There are limited data in the literature on melt processing of crystalline ceramics; particularly regarding the impact of reducing atmosphere on phase formation in melt derived materials. A composition of CW-AFHZ targeting hollandite, perovskite, and zirconolite was fabricated by a melt and crystallization process in a 1%H_2 balance Ar gas atmosphere. Processing in a reducing atmosphere was expected to result in metallic Mo, and enhanced Cs incorporation into the hollandite structure. Insight into oxygen partial pressure (PO_2) values needed to reduce Mo in an oxide melt were obtained from previous work by Schreiber, et al.[17, 18] Figure 3-7 shows the SEM determined microstructure and local composition of phases which are summarized in Table 3-8. The targeted hollandite, perovskite, and zirconolite phases were observed along with alumina, powellite, and a Cs-Mo phase. These initial attempts to process waste forms from CSLNTM-High Mo waste streams in a reducing atmosphere were not successful in producing fully reduced molybdenum. It should be noted however that a starting precursor of MoO_3 was used instead of Mo metal or a solution of metal nitrates, which would be the likely stream from the separation unit operations.
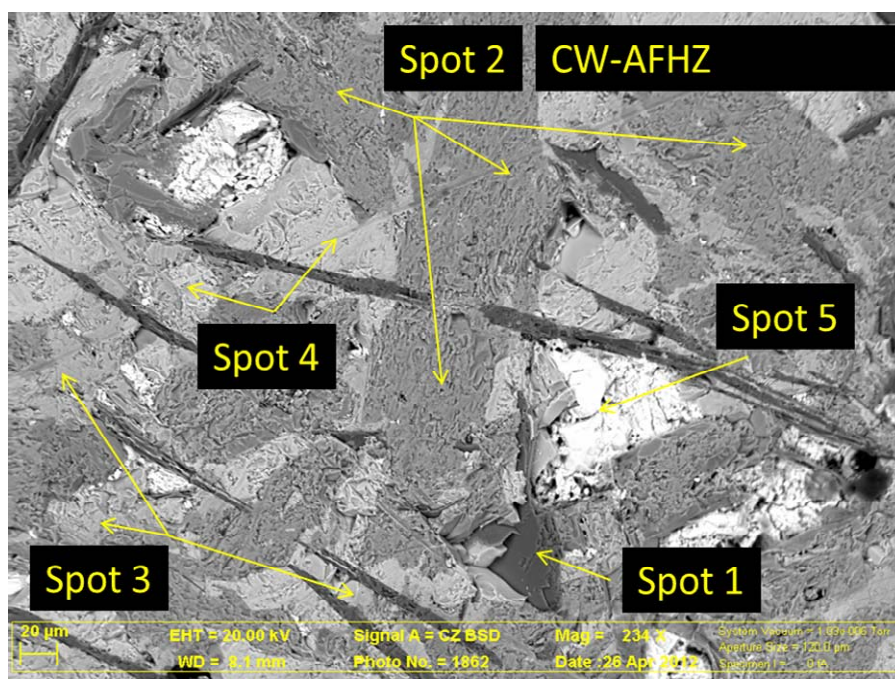

Figure 3-7.   CW-AFHZ Fabricated by Melting and Crystallizing in 1%H_2 balance Argon-Backscattered Electron Micrograph

Table 3-8. CW-AFHZ Fabricated by Melting and Crystallizing in 1%H$_2$ balance Argon-Summary of Elements and Crystalline Phases (*Crystalline phases determined from XRD measurements and EDAX elemental analysis*)

Spot	Elements (Major, Minor)	Crystalline Phases*
1	O, Al	Al$_2$O$_3$
2	O, Ti, Al,Ba	Hollandite- BaAlTi$_5$O$_{14}$
3	O,Ti, Zr,Ca	Zirconolite-CaZrTi$_2$O$_7$
4	O,Ti, Ca,Nd	Perovskite- Nd doped CaTiO$_3$
5	O, Cs, Mo, Ca, Ba	Cs$_2$MoO$_4$ + (BaCa)MoO$_4$

In addition, carbon-based reductants (sucrose) added to the CW-AFHZ composition processed in a reducing atmosphere displayed similar a phase assemblage, notably the presence of a Cs-Mo phase. The Cs affinity for the Mo oxide phase clearly presents a problem for achieving the targeted phase formation. Hollandite materials are typically produced by calcination followed by long duration sintering steps at temperatures near 1200 $^\circ$C. The melt processing of single phase Cs containing hollandite is not well established and there may be additional kinetic barriers to Cs incorporation. Melt processing is distinct from long duration sintering processes. In fact, fractional crystallization was observed in zirconolite CaZrTi$_2$O$_7$ with multiple phases forming upon cooling from the melt. A Zr rich ZrTiO$_4$ phase initially formed resulting in Zr-poor zirconolite, which eventually decomposed into rutile, perovskite and defect rich zirconolite phases. Heat treatment procedures including quenching, controlled cooling, and intermediate temperature annealing after cooling from the melt should be explored to achieve phase equilibrium.

4. PROPOSED REFERENCE CERAMIC COMPOSITION

4.1.   *CS/LN/TM High Mo, or No Mo*- Target Waste Stream

Due to the difficulty with Cs-Mo oxide formation, processing should be performed in a reducing environment targeting metal Mo. Therefore the targeted composition for Mo and No Mo waste streams is the same as indicated in Table 4-1. Powellite has been removed from the list of targeted phases. CaO additions are added to react with ZrO$_2$ in the waste, resulting in zirconolite. Iron oxide (5.82 wt %) is proposed as the baseline additive targeting hollandite phase formation. Alternative transition metals such as Co, Zn, Cr, are also potential additives to facilitate Cs incorporation into the hollandite phase.[13, 19]

Table 4-1. Reference Ceramic Composition (wt %) for CSLNTM-High Mo and No Mo Waste Streams *Fe or multivalent transition metal (Co, Zn, Cr) to assist hollandite formation[13, 19]

Composition	CW-AFHZ-NoMo	Targeted Phase
Waste	23.74	
Al$_2$O$_3$	6.62	Hollandite
TiO$_2$	51.03	Hollandite, Perovskite, Zirconolite
CaO	1.36	Zirconolite
BaO	11.43	Hollandite
*Fe$_2$O$_3$	5.82	Hollandite

4.2.   CS/LN/TM No Mo, Zr- Target Waste Stream

Hollandite and perovskite phases are targeted for the CSLNTM with no Mo and no Zr with the waste form composition given in Table 4-2. Initial melt and crystallization processing of this composition in air resulted in Cs-Ti phase formation and limited incorporation into the hollandite. However, processing modifications including melting in a reducing atmosphere and post melt annealing steps are anticipated to improve the targeted elemental partitioning.

Table 4-2. Reference Ceramic Composition (wt %) for CSLNTM- No Mo, Zr Waste Streams *Fe or multivalent transition metal (Co, Zn, Cr) to assist hollandite formation[13, 19]

Composition	CW-AFH-No Mo, Zr	Targeted Phase
Waste	22.62	
Al_2O_3	7.21	*Hollandite*
TiO_2	51.38	*Hollandite, Perovskite,*
BaO	12.45	*Hollandite*
*Fe_2O_3	6.34	*Hollandite*

5. PATH FORWARD

Perovskite and zirconolite phases are readily formed from a melting and crystallization process with demonstrated durability of Zr, and M^{+3} lanthanide elements, both in air and reducing environments.[10] Waste streams that contain Mo must be produced in reducing environments to avoid Cs-Mo oxide phase formation. Waste streams without Mo have the ability to be melt processed in air. Hollandite based on the general structure of $BaAl_{1.46}Fe_{0.8}Ti_5O_{14}$ has been observed to form from this process, however Cs is often seen to partition to additional phases including Cs-Mo and Cs-Ti. The immediate focus will be on Cs incorporation into the hollandite structure through targeted single phase studies investigating the impact of processing conditions including melting in reducing atmospheres and post melt heat treatment steps. Current formulations are based on alumina and iron oxide additions targeting Cs incorporation through improvements in the hollandite structure. It is possible that other transition metals may be more appropriate and the targeted hollandite stoichiometry may differ under oxidizing or reducing conditions. Collaborations on this topic are planned with researchers at the Australian Nuclear Science and Technology Organization (ANSTO) who have performed work on melt processing of single phase Cs containing hollandite structures.

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