A New Paradigm for Understanding Multiphase Ceramic Waste Form Performance

Fuel Cycle Research and Development

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1 Executive Summary

This project fabricated model multiphase ceramic waste forms with processing-controlled microstructures followed by advanced characterization with synchrotron and electron microscopy-based 3D tomography to provide elemental and chemical state-specific information resulting in compositional phase maps of ceramic composites. Details of 3D microstructural features were incorporated into computer-based simulations using durability data for individual constituent phases as inputs in order to predict the performance of multiphase waste forms with varying microstructure and phase connectivity. 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. A major technical hurdle to the use of multi-phase oxide waste forms is the ability to characterize the complex elemental partitioning that occurs, particularly at the grain boundary interface in crystalline systems, as well as to predict the long-term performance of these material systems. This work aimed to systematically fabricate and characterize multi-phase waste form compositions with varied microstructures followed by advanced 3D characterization of their interconnected network, including residual porosity. Material system modeling incorporating the elemental release and the interconnected microstructural network of phases was performed to better understand the material systems’ performance and degradation.

Hollandite (Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$) and pyrochlore (Nd$_2$Ti$_2$O$_7$) were selected as model material systems. Hollandite compositions containing Ga as a dopant were chosen due to favorable X-ray absorption characteristics, redox stability and reported decreased in the processing temperature. Synchrotron-based transmission x-ray microscopy was used to image the 3-D microstructure of multiple phases within model waste form material systems. It was found that Ga doping levels consistent with those commonly used for nuclear waste immobilization (Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$) could be readily imaged. In addition, the 3-D morphology and elemental distribution of Ga and Nd within model multiphase waste form materials consisting of varying volume fraction mixtures of Hollandite (Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$) and pyrochlore (Nd$_2$Ti$_2$O$_7$) were evaluated. The results obtained by this analysis suggest that differential X-ray absorption contrast tomography is appropriate for the analysis of the major phases found in these model waste form systems. Distinct phases within each sample were identified based on their relative compositions of Ga and Nd. Additional analysis including SEM-EDS confirmed the heterogeneous nature of chemical composition existing in these materials. Three-dimensional absorption contrast images of the samples exhibited contrast changes across the Ga k-edge consistent with the SEM-EDS findings. The analysis suggests that the minority phase is a different stoichiometry/composition of the primary hollandite phase formed by the solid-state ceramic processing.

The modeling effort developed multi-physics models set on the actual as-manufactured microstructure of the heterogeneous waste form materials being developed in this program as a
foundation for maximizing the functional performance and estimating the durability and life based on the microstructural parameters and constituent properties that define the materials, and the changes in those parameters and properties caused by the combined effects of mechanical and chemical degradation during their life. The present work constructs a “critical path” concept that generalizes the familiar concept of percolation to create a broad foundation for predicting transitions in physical properties and performance that often define design boundaries or performance transitions that signal the onset of unsteady behavior such as fracture or chemical breakdown. Ultimately, the “critical paths” of flux that develop are determined by the morphological details and by the vector gradients of the concentration in various directions, as well as by the details of the diffusion properties of the individual phases.

2 Project Objectives

The overall project objectives were to systematically fabricate and characterize multiphase waste form compositions with varied microstructures followed by advanced 3D characterization of their interconnected network, including residual porosity. Material system modeling was focused on the impact of microstructure including details of the interconnected microstructural network of phases to better understand the material systems’ performance and degradation. The project was organized into three tasks to accomplish these goals: i) Task A Materials Selection, Processing and Performance Evaluation, ii) Task B Advanced 3D Characterization and iii) Task C Development of Microstructure-based Multiphysics Models.

Task A focused on processing approaches to create multiphase ceramic waste forms with controlled microstructure and chemical compositions and to develop high-fidelity approaches to characterize and quantify the microstructure of the multiphase ceramics. Materials selection was performed including identifying the best model “binary” mixtures of phases representing simplified waste forms using the most prevalent element from the waste stream as a dopant. Task B focused on advanced characterization of the 3D structure of multi-phase ceramic waste forms principally utilized using full-field, x-ray computed tomography performed on synchrotron-based transmission x-ray microscopes. Task C focused on developing insights into the long-term performance of multiphase ceramic waste forms by developing durability models that mechanistically combine the effects of mechanical and chemical degradation (especially corrosion as a function of microstructure, using data from Task A and B in years two and three). The following sections provide a background on materials and methods followed by results and key findings.

3 Background

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. These materials, originally developed by Ringwood et al., are often referred to as SYNROC (short for “Synthetic Rock”). SYNROC materials comprise ceramic waste forms that are tailored to mimic certain minerals (i.e., unique crystalline structures) that are known to host radionuclides by binding them into specific crystalline networks.
design of ceramic waste form materials is guided by knowledge of naturally occurring minerals, which contain radioactive and non-radioactive elements in waste generated from used nuclear fuel (UNF) reprocessing and weapons production.\textsuperscript{5,6}

In an aqueous reprocessing scenario, four primary waste streams are typically considered: i) a Cs/Sr separated stream, ii) a waste stream consisting of lanthanide fission products, iii) a transition metal fission product waste stream resulting from transuranic extraction, and iv) residual, un-recovered minor actinides.\textsuperscript{7,8} Many of the elements in the aqueous reprocessing waste stream are known to react with select additives to form stable SYNROC (titante-based) crystalline phases of the types hollandite,\textsuperscript{9,10} perovskite, pyrochlore, and zirconolite.\textsuperscript{11} These materials are typically densified via hot isostatic pressing (HIP). Recent work, however, has shown that they can also be produced from a melt.\textsuperscript{6}

A greater understanding of processing conditions on the elemental partitioning, microstructural features, and connectivity of the phases is needed to better design and exploit the properties of ceramic waste forms. Moreover, the impact that 3-D features of a material’s microstructure have on its corrosion behavior is needed to assess long-term waste form performance. For instance, residual porosity that is connected to the material’s surface increases the effective surface area available for corrosion. Similarly, in multiphase systems, the preferential corrosion of a particular phase may lead to an increase in porosity and effective surface area. In both cases, the 3-D distribution of phases (including the pores) is central to gaining an improved understanding of the link between microstructure and corrosion behavior in multi-phase waste form materials.

Central to gaining an improved understanding of the connection between 3-D features of a waste form material’s microstructure and its corrosion behavior are microstructural imaging techniques. Of particular importance are those techniques that, at a minimum, have the capability to (1) discern multiple material phases and to (2) reveal each phase’s spatial distribution, morphology, and connectivity in 3-D.

A number of 3-D imaging techniques exist that meet the basic criteria listed above. Examples include, but are not limited to, magnetic resonance imaging (MRI), transmission electron microscope (TEM) tomography, scanning electron microscopy (SEM)-based stereology, focused ion beam-scanning electron microscope (FIB-SEM) serial sectioning, and x-ray tomography. In recent years, all of these techniques (along with a number of others) have seen increasingly rapid development and widespread application in the study of “energy materials” (i.e., materials used in energy conversion and storage technologies).\textsuperscript{12,13} Similar to SYNROC, energy materials design stands to benefit from an improved understanding of how 3-D microstructural features influence material performance.

In choosing a 3-D technique to study ceramic waste form materials, two additional criteria are required. The technique must be (1) capable of imaging dense (i.e., high Z) materials and it must (2) offer 3-D resolution on the order of ten’s of nanometers with a field of view large enough to capture material volumes on the order of hundreds of cubic microns. Under these
conditions, two direct, 3-D imaging techniques – FIB-SEM serial sectioning and synchrotron-based x-ray nanotomography (XNT) – are particularly suitable.

FIB-SEM serial sectioning, a widely accessible and applied technique, produces a 3-D microstructural image by successively imaging and then milling away consecutive, thin slices of material.\[^{12}\] The sample is destroyed during the imaging process. By exploiting secondary electron contrast using specialized detectors, FIB-SEM is able to discern multiple material phases. The technique’s spatial resolution is determined by the 2-D resolution of the SEM (typically single nanometer) and the thickness of each milled slice (often slightly less fine than the SEM resolution, e.g., \(~5\text{–}10\) nm). The volume of material that can be imaged using FIB-SEM is relatively large (\(~1000\)’s of nm\(^2\) field of view) compared to XNT (whose field of view is \(~100\)’s of nm\(^2\)). Finally, the technique may be performed in conjunction with the SEM’s complimentary imaging modes (for example, EDX for chemical mapping in 3-D).

Synchrotron-based XNT makes use of a transmission x-ray microscope (TXM) with a synchrotron x-ray source to perform tomography at 3-D resolutions on the order of 10’s of nanometers (e.g., \(~20\text{–}50\) nm).\[^{12}\] Synchrotron sources are typically housed in government-run facilities that award prospective users “beam-time” through a competitive proposal submission process. As a result, synchrotron-based XNT is less accessible than FIB-SEM. Different material phases are distinguished in XNT by exploiting characteristic x-ray absorption behavior of elements within the phases. Relative to FIB-SEM, XNT generally offers a smaller field of view (100’s of nm\(^2\) as compared to 1000’s of nm\(^2\)), which means that a smaller volume of material may be considered at a time (although progress is being made in increasing the volume that can be imaged). In contrast to FIB-SEM, XNT is non-destructive, which makes possible the analysis of a single sample by a variety of complimentary techniques, e.g., electron-based imaging or other x-ray methods, such as x-ray fluorescence. Like the SEM, the synchrotron-based TXM, which provides tunable x-ray energy, has a variety of imaging modes that can be used in conjunction with tomography (for example, x-ray absorption near-edge structure XANES spectroscopy to determine chemical bonding states). In contrast to the FIB-SEM’s electron beam, hard x-rays exhibit negligible attenuation in a variety of gas atmospheres, which eliminates the need for an evacuated sample chamber. This, along with XNT being non-destructive, makes the technique more readily applicable (as compared to FIB-SEM) for \textit{in situ} imaging.

Once the microstructural parameters are examined, their influence on charge transport behavior needed to be investigated to understand the contribution of these variations on overall flux of nuclides out of the systems. To study these characteristics to design an efficient waste form, experimental methods have proven to be costly and time consuming. Also different leaching experiment such as Single Pass Flow Through (SPFT) Test – ASTM C1662, MCC-1 Static Leach Test – ASTM C1220, Solution Replacement Test, Product Consistency Test (PCT) – ASTM C1285 and Vapor Hydration Test (VHT) – ASTM C1663 only provides information about the performance of the waste form for a short period of time in comparison to reference materials, typically standard borosilicate glass. The current suite of testing and analysis does not provide information about the mechanism of corrosion, the performance of the waste form as a
function of microstructure and morphology and ultimately the performance over geological timescales. Finite element analysis of these systems to determine optimum microstructure, phase combinations and mixture ratio can facilitate the design process by reducing time and cost. Finite element analysis is now widely used to investigate electrochemical systems. In this work, a finite element model of waste form system is used to simulate radionuclides ion transport in the system. This model can be used to resolve both 2D and 3D domains representing ideal or real microstructures of a waste form system.

To introduce the multiphysics discussion into this context, we appeal to the established approach to modeling combined physical degradation effects on the life of polymer membrane fuel cells (PEM cells), along with more recent predictions of ceramic composite durability. For example, if our observable is strength, and the precipitous drop of strength that is common in such devices defines end of life, we have shown that an acceptable response equation can be formulated. Finally, the life of the element was predicted in terms of number of cycles of hydration. So the physics of that situation involved mechanical and thermal fatigue, thermal and chemical creep, and chemical degradation, and life was successfully predicted for many operating conditions. Many other such examples have been generated over the years in the general literature.

4 APPROACHES AND RESULTS

4.1 Methods

4.1.1 Synthesis of Hollandite Powders

Three hollandite compositions were considered: (i) \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \) (no Cs); (ii) \( \text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16} \) (highest Cs content); and (iii) \( \text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16} \) (intermediate Cs content typically found in the literature). The hollandite was synthesized by solid-phase reaction. \( \text{BaCO}_3, \text{Cs}_2\text{CO}_3, \text{Ga}_2\text{O}_3, \) and \( \text{TiO}_2 \) (all from Sigma-Aldrich, St. Louis, MO, USA; >99.9%) were mixed in stoichiometric proportions and then ball-milled in ethanol with \( \text{ZrO}_2 \) milling media for 24 h. The powders were dried and calcined at 1200°C for 10 h to form the hollandite phase. Hollandite pellets were prepared by uniaxially pressing hollandite powders and then sintering them at 1300°C for 2 h to densify the resulting composite. (Due to the sintering activity of \( \text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16} \) and \( \text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16} \), it was not possible to prepare a completely dense sample.) For the dense, two-phase hollandite–\( \text{TiO}_2 \) system, 20 wt% \( \text{TiO}_2 \) was added to the hollandite powder, the mixture was ball milled, and then sintered at 1300°C for 2 h. For the porous, two-phase hollandite–\( \text{TiO}_2 \) sample, 10 wt% graphite was added as a pore former.

The hollandite \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \), and pyrochlore \( \text{Nd}_2\text{Ti}_2\text{O}_7 \) powders were synthetized by traditional solid state reaction. \( \text{BaCO}_3, \text{Ga}_2\text{O}_3, \) and \( \text{TiO}_2 \) raw powder for \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{4.34}\text{O}_{16} \) and \( \text{Nd}_2\text{O}_3 \) and \( \text{TiO}_2 \) for \( \text{Nd}_2\text{Ti}_2\text{O}_7 \) were mixed in stoichiometry by ball milling for 24 h. Then the mixed powders were pressed into pellets and calcined at 1200°C for 10 h and 2 h separately.
Then hollandite $\text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16}$ (density 4.3 g cm$^{-3}$), and pyrochlore $\text{Nd}_2\text{Ti}_2\text{O}_7$ (density 6.098 g cm$^{-3}$) powders were mixed at volume fraction of 50:50, and ball milled for 24 h. Then the mixed powder was pressed (100 MPa) into green pellets and sintered at 1300°C for 30 min to achieve 95% density or 1250°C for 2 hours to achieve 70% density.

4.1.2 Development of TXM work

Synchrotron-based differential x-ray absorption contrast nanotomography makes use of a transmission x-ray microscope. Upstream from the microscope, a synchrotron x-ray source and monochromator provide the TXM with a monochromatic beam of x-rays, which is directed by a capillary condenser through a pinhole and onto the sample, which sits on a rotation stage and is fully illuminated by the beam (as opposed to a configuration in which a small-diameter beam scans across the sample). The x-rays transmitted through the sample are focused onto a CCD x-ray detector by a Fresnel zone plate. A three-dimensional image of a sample is obtained by rotating it and collecting images at small angular increments. The series of 2-D images, called “projection images,” are then “tomographically reconstructed” to yield a 3-D image of the sample. Contrast in TXM images reflects variations in the linear x-ray absorption (or “x-ray attenuation”) coefficients of the elements within the sample. The absorption coefficient is a material property, which in Beer’s Law determines the proportion of an incident x-ray’s energy that is absorbed as it passes through a given length of material. Thus, darker regions in a TXM image correspond to locations within the sample that contain elements with greater attenuation coefficients. In this work, the images are presented in so-called “reverse contrast mode” whereby the opposite of the previous statement is true, i.e., darker regions indicate the presence of elements with smaller attenuation coefficients. Modeling of the material’s absorption behavior was performed using the CXRO X-ray absorption calculator assuming a 20 μm thick specimen approximating the dimensions of samples to be used for imaging experiments. A 5-10% change in transmission intensity across an absorption edge is considered appropriate for the detecting the presence of the phase with 30 nm spatial resolution.

Cylindrical samples of the waste form materials for tomographic x-ray imaging were ion-milled using a focused ion beam-scanning electron microscope (FIB-SEM) with a Ga ion beam (Hitachi). The cylinders were approximately 15 μm in diameter and between 15-20 μm in height. They were Pt-welded onto the tips of watch pins, which could then be mounted in the TXM at Beamline 6-2 at the Stanford Synchrotron Radiation Lightsource. Single phase hollandite samples and hollandite/TiO$_2$ samples were imaged above (10.400 keV) and below (10.334 keV) the Ga k-absorption edge (10.337 keV). The voxel size of the collected images was 40.29 nm. The images were segmented using a watershed algorithm implemented in MATLAB and the segmented volumes were visualized using Avizo.

The Nd$_2$Ti$_2$O$_7$ samples were imaged above (6.241 keV) and below (6.175 keV) the Nd L$_3$-absorption edge (~6.21 keV). The model dual phase waste form samples containing both materials were imaged above and below both the Nd L$_3$ and Ga K-absorption edges.
4.1.3 SEM, TEM, Advanced Characterization
The samples’ phase structures were characterized by X-ray diffraction (Rigaku TTR-III; Rigaku, Woodlands, TX, USA) using CuK radiation (D/Max-gA) with 2θ from 10° to 70° using a scan rate of 1° per min. Each hollandite sample’s morphology was observed using a scanning electron microscope (SEM; Hitachi SU-6600; Hitachi, Schaumburg, IL, USA) and their chemical compositions were confirmed using an energy-dispersive spectrometer (EDS, Oxford, Abingdon, UK). Prior to EDS measurements, samples were polished using different polishing media with mesh number from 600 to 1200. Point-based EDS analysis was used to estimate hollandite chemical composition was performed at 10 different points in both the majority and minority hollandite phases. X-ray photoelectron spectroscopy (XPS, Axia Ultra DLD, Karatos analytical Ltd, Manchester, UK) was used to determine the surface compositions of hollandite.

The 3D phase connectivity was obtained were collected using a FEI dual-beam 400-S FIB system (Hitachi). The FIB milling was performed with a Ga+ ion-beam current of 460 pA at 30 kV. For SEM imaging, a magnification of 12 kX and a through the Lens Detector operating in Backscatter Electron (BSE) mode at a low scan rate were employed. Data processing followed the steps of i) alignment of the consecutive slices, ii) correction of the dimensions taking into account the tilt of the electron beam, iii) thresholding of the grey levels and labeling of phases, and iv) 3D image generation. The remaining drift components of the electron beam in the x and y directions were corrected by applying least square fitting algorithms to achieve image alignment. Finally, the resulting volume was cropped to retain the features common to all slices. The absolute dimensions in the x direction were obtained from a calibrated SEM magnification.

4.1.4 Multiscale Modeling
To calculate the flux of stored nuclear ion through the waste form structure, we used Nernst-Planck flux equation. This equation describes transport of chemical species by convection, migration and diffusion through electrolyte membrane. Nernst-Planck equation has been used to model different charge transport phenomenon. The Nernst-Planck equation based model can be used to calculate concentration gradient, species flux, potential gradient of the system. Equation 1 shows Nernst-Planck equation

\[ N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi + c_i u \]  (1)

\[ N_i = \text{Flux of species, } i (\text{mol/m}^2\cdot\text{s}) \]
\[ D_i = \text{Diffusion co-efficient (m}^2/\text{s}) \]
\[ c_i = \text{Concentration of ion, } i (\text{mol/m}^3) \]
\[ z_i = \text{Valance of species} \]
\[ u_{m,i} = \text{mobility (s/mol/kg)} \]
\[ F = \text{Faraday constant} \]
\[ \phi_i = \text{Electrolyte Potential} \]
\( \mathbf{u} = \text{velocity vector (m/s)} \)

In the case of a solid structure velocity term \( u_i \) is ignored. As no potential is applied across any of the boundaries the migration term is ignored. In this study, we also did not consider the potential difference created by the space charge due to the defects accumulated at the grain boundaries. But if required this potential can be applied to the model using internal boundary condition. For this case of solid waste form, Cesium release will be controlled by the diffusion coefficient of the species through the waste form medium and driven by the concentration gradient of the species. The amount of Cesium released can be obtained by calculating the total flux using equation 1. Transient solution of the equation calculates flux over time that can be used to obtain the leaching rate of Cesium.

Domain diffusion co-efficient was obtained from reported ionic conductivity of Cesium in hollandite structure. Nernst-Einstein relation is used to calculate the diffusion co-efficient described by Equation 2.

\[
\sigma = \frac{z_i^2 e^2 c_i}{k_B T} D_i 
\]

Where, \( D_i = \text{Diffusion co-efficient (m}^2/\text{s)} \)
\( \sigma = \text{Ionic Conductivity} \)
\( z_i = \text{Valance of species} \)
\( c_i = \text{Concentration of ion, i (mol/m}^3 \)\)
\( k_B = \text{Boltzmann’s constant} \)

The Nernst-Planck equation is solved using Nernst-Planck Equation Module of COMSOL Multiphysics. Both 2D and 3D structure can be used as the material domain in this model. For conformal analysis with real microstructure, computational domain can be generated from 3D scans of the material using Transmission X-ray Microscopy (TXM).

4.2 Results and Key Findings

4.2.1 Single Phase hollandite TXM results

Three Ga-containing, single-phase hollandite compounds were studies: (i) \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \) (no Cs), (ii) \( \text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16} \) (intermediate Cs content) and (iii) \( \text{Ba}_{0.66}\text{Cs}_{0.66}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16} \) (highest Cs content). These compositions were intended to provide insight into the phase formation and microstructural evolution of pure Ba hollandite and of hollandite with varying amounts of Cs. Owing to its simplicity and prevalence in realistic multi-phase waste forms, titanium oxide (TiO\(_2\)) was selected as the second component for the model two-phase systems. The hollandite-TiO\(_2\) materials were fabricated in both dense and porous forms in order to evaluate the ability of the imaging technique to discriminate residual porosity.

It is important to note that the concentration of Ga within a Ga-containing phase influences the magnitude of the contrast change observed in images collected above and below
Ga’s k-edge: in general, the higher the Ga concentration, the greater the contrast change. The magnitude of the characteristic change in contrast depends on Ga’s concentration within a phase has an important implication for it identification: phases will be discernable within a material’s volume as long as their relative Ga contents are sufficiently different. In other words, if two phases are to be distinguished, it is not necessary for one to contain Ga and the other to be completely devoid of the element; they can both contain Ga as long as the concentration of Ga within each is sufficiently different to produce a clearly observable contrast change when the phases are imaged on either side of the absorption edge. As it turns out, it appears that nearly all of the material phases encountered in the materials examined for this milestone contained Ga. The concentration of Ga within each, however, was significantly different so that the phases could be distinguished by differential x-ray absorption contrast tomography.

Figure 4.1 presents the XRD pattern of $\text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16}$ (no Cs), $\text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16}$ (relatively high Cs content), and $\text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16}$ (intermediate Cs content). The patterns show that $\text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16}$, $\text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16}$, and $\text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16}$ are all single-phase hollandite. All XRD lines were indexed in the $I4/m$ space group (tetragonal structure) and no parasitic phases were detected. Structural features including lattice parameters were reported in previous work.$^{21,22}$ Due to the larger size of the Cs$^+$ ion compared to the Ba$^{2+}$ ion, increasing Cs concentration resulted in an increase of the $a$ lattice parameter but with negligible changes to the $c$ lattice parameter.

**Figure 4.1.** XRD patterns for dense hollandite samples synthesized by sintering at 1300 °C for 2 h.
As explained previously, the single-phase, waste form materials of varying composition were doped with Ga. By performing differential x-ray absorption contrast tomography on samples of the baseline material (a hollandite phase devoid of Cs), the two hypotheses that are relevant to evaluating the use of Ga-doping as a means to identify the hollandite phase in x-ray images could be tested. Recall that the magnitude of a phase’s contrast change in images collected across the Ga k-edge depends on the Ga concentration within the sample. If the hollandite phase did not contain a sufficient amount of Ga dopant in the structure, then the contrast change could potentially be too weak to clearly identify hollandite in subsequent studies of more complex, multi-phase systems. Furthermore, the value of Ga in marking the hollandite phase would also be compromised if its incorporation into the phase were inhomogeneous; in which case the contrast change exhibited by hollandite would be non-uniform. Thus, imaging the baseline compositions without Cs provided a means of confirming that Ga-doped hollandite exhibits a uniform contrast change that is significant enough to clearly identify the phase.

Two samples of baseline material were imaged. Figures 4.2 present an example projection image and representative, reconstructed cross-sections collected at each photon-energy above and below the Ga k-edge for each sample. The images in Figure 4.2 reveal that the first sample was in fact largely homogeneous and comprised a single hollandite phase. Furthermore, the pixel intensity for the hollandite phase changed significantly across the k-edge (~10% increase), which suggests that Ga-doping can provide an effective means of marking hollandite phases in x-ray images of waste form materials.

Figure 4.2. (a) Projection images of a baseline single-phase hollandite waste form sample (Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$) imaged below the Ga k-edge. The location of three cross-sections of the
material shown in (b-d) are marked on the projection image in (a). Panels (e-h) show the same regions of this sample imaged above the Ga k-edge. Note that the vast majority of the sample volume is a uniformly Ga-doped hollandite phase with some small Ga-rich regions and porosity. The contrast change and, for the most part, uniform incorporation of Ga into the hollandite provide evidence that Ga is a useful elemental marker that can be used to discern multiple phases in waste form materials imaged by TXM techniques.23

Like the images of the baseline samples, images of the Cs-containing samples, shown in the second and third columns revealed a non-uniform distribution of Ga. There is, however, in addition to the globular Ga-rich regions, another type of Ga variation: namely, rod-like regions of Ga content higher than the majority of the material volume (~35% contrast change versus a ~10% contrast change across the edge) but less than that of the globular regions (which exhibited a contrast change of ~48% across the edge). Both types of regions were in the intermediate Cs-content sample and can be seen in the 3-D renderings shown in Figure 4.3 and 4.4 where the Ga-rich, globular regions are shown in green and the rod-like “minority hollandite” in red. The “majority hollandite” is shown in blue and has been rendered transparent such that the porosity, the green, and the red phases are viewable. The porosity accounted for ~11% of the imaged volume of the intermediate Cs-content sample. In the higher Cs sample, all Ga-rich regions were rod-like and accounted for approximately 3% of the sample volume (with porosity about 13%).

![Figure 4.3](image_url)

**Figure 4.3.** A 3-D rendering of the primary hollandite phase (in blue) and the possible secondary phase (in red) that are observable in the cross-sections of the high Cs-content sample (Ba0.667Cs0.667Ga2Ti6O16). The sample’s porosity is also visible in the rendering, which are the unfilled regions of the cube. The darker blue regions mark the interfaces between void space and
the hollandite phase, which has been rendered to resemble a semi-transparent “gelatin”. The secondary phase (in red) exhibits a distinct rod-like morphology.\textsuperscript{23}

**Figure 4.4.** A 3-D rendering of the intermediate Cs-content, single-phase hollandite sample ($\text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16}$). A rod-like structure of the possible secondary phase is clearly visible in red.\textsuperscript{23}

The hollandite phase is shown in blue. The darker blue regions mark the interface between the hollandite phase and void space. The red surfaces that coat the porosity in some areas are artifacts, which can be removed by more refined segmentation procedures.

In summary, the imaging studies on single-phase hollandite waste form materials performed for this milestone suggests that Ga is a suitable doping element to provide a means to discern primary and secondary phases in waste form materials using the TXM. A natural extension of this work would be to perform x-ray absorption near-edge spectroscopy (XANES) at the Ga k-edge in order to obtain information about the chemical bonding state of Ga within the phases. The use of Ga to discern various phases within waste form materials, however, is not limited to single-phase materials. The results demonstrate that Ga is an effective dopant in making multiple phases discernable by synchrotron-based x-ray imaging methods, in this case, differential x-ray absorption contrast tomography. The next set of preliminary results show images of two-phase, hollandite/TiO\textsubscript{2} waste form systems. In these images, the primary hollandite and TiO\textsubscript{2} phases are discernable from one another, and, in addition, there appear to be multiple secondary phases, which are clearly seen in the reconstructed cross-sections.

**Dense Hollandite/TiO\textsubscript{2}**

Figure 4.5 shows example projection images and reconstructed cross-sections obtained at each energy level for the dense hollandite $\text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16}/\text{TiO}_2$ sample. The hollandite
phase is clearly discernable from the TiO$_2$, thereby confirming our hypotheses. A slight contrast change exhibited by the TiO$_2$ indicates that Ga incorporated into both the TiO$_2$ and the hollandite phase. Aliovalent Ga doping, Ga$^{+3}$ on Ti$^{+4}$ sites is well known in these materials and low Ga levels in TiO$_2$ resulting from diffusion during high temperature sintering were expected to some degree. A very small region of higher Ga content is observable in cross-section 1. This region is located at the sample’s perimeter and has a sphere-like morphology. Also in cross-section 1 is a thin region along the sample’s perimeter that appears to be an artifact of milled material that was re-deposited onto the side of the sample or Ga ion implantation during the fabrication process using the FIB-SEM. As is the case for the single phase hollandite system, the results on the hollandite + TiO$_2$ systems presented in this report show that Ga can be used to discern multiple phases in waste form materials imaged by synchrotron-based x-ray techniques.

**Figure 4.5.** Example projection images and cross-sections obtained from a dense hollandite Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$/TiO$_2$ material. The hollandite is clearly discernable from the TiO$_2$. Because the TiO$_2$ exhibits a contrast change, it must contain some Ga. A very small region of higher Ga density material is observable in cross-section (1). As was the case with other Ga-rich regions, it is close to the sample’s perimeter. Pt, which is seen in cross-section 2, was used to weld the samples to the pins that were mounted into the TXM. $^{23}$

Further analysis of these rod-like Ga-rich regions is provided in just after the presentation of the results for the two-phase waste form systems. In the additional analysis, a combination of electron-based microscopy, spectroscopy, and additional analysis of the x-ray images suggest
that the “majority” and “minority hollandite” phases are a local variation in the composition of the single-phase hollandite. The rod-like microstructure of the minority hollandite which was found to be Cs and Ga rich is consistent with literature reports of enhanced growth along the [100] tunnel direction in hollandite with increasing Cs content. Before proceeding to that analysis, however, the remainder of this section presents the x-ray imaging results for the two-phase model waste-form systems, which were intended to demonstrate the ability of the technique to discern two solid phases from pore in waste form material systems.

Figure 4.6. 3-D visualization of the single-phase hollandite (a) without Cs ($\text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16}$), (b) with intermediate Cs content ($\text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16}$), and (c) with high Cs content ($\text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_{2}\text{Ti}_{6}\text{O}_{16}$). Panel (d) shows the two types of differing Ga-content regions found in the samples. The rod-like region in the upper panel was isolated from the higher Cs-content sample and the globular region was taken from the baseline sample without Cs. The intermediate Cs sample is the only one of the three that contains both types of regions.\(^{23}\)

The images of the two-phase model systems demonstrate the ability of the x-ray imaging technique to discern many regions of varying Ga concentration. In order to fully understand the imaging results, however, additional complementary analysis is required. In the following section, further analysis of the rod-like Ga-rich phase observed in the Cs-containing single-phase hollandite samples is performed that leads to additional insight into the composition of the phase.

4.2.2 Spatially Resolved Chemical Composition

Majority & Minority Hollandite Phases

As pointed out in the TXM result, the rod-like Ga-rich phase occupied ~2% and 3% in the intermediate and high Cs-content hollandite samples, respectively. The XRD results
presented earlier, however, did not reveal any secondary phases within the detection limit of the technique. This is likely because the detection sensitivity of the XRD technique is approximately 5% volume fraction. SEM-EDS analysis of these samples also did not reveal significant elemental partitioning or segregation to indicate secondary phase formation. Together, these results suggest that the Ga-rich phase observed in the TXM images could be a single hollandite phase with a regions of varying Ga content.

In order to confirm the composition of the Ga-rich phase, SEM-EDS was employed to analyze \( \text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_2\text{Ti}_6\text{O}_{16} \) and \( \text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16} \) pellets, as shown in Figure 4.7. In the mapping result, Ba, Cs, Ti, and O were distributed uniformly on the surface. However Ga exhibited bright spots in the elemental maps. These brighter signals indicate a higher elemental ratio, which is consistent with the TXM result. Estimates of the Ga-rich areas were obtained by EDS from various points as shown in Figure 4.8. The EDS point results were recalculated normalizing to Ti (i.e., the Ti stoichiometry was set as the target value). The calculated results are displayed in Table 4.1.

![Figure 4.7](image-url) The SEM-EDS mapping images of a) \( \text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_2\text{Ti}_6\text{O}_{16} \) (higher Cs content) and b) \( \text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_{2.32}\text{Ti}_{5.68}\text{O}_{16} \) (intermediate Cs content).
Results for the Ba$_{0.667}$Cs$_{0.667}$Ga$_2$Ti$_6$O$_{16}$ sample (the higher Cs-content) indicate that the stoichiometry of Ba, Cs, and Ga in the majority phase was 0.633, 0.592 and 1.93 respectively, which is close to the target values 0.667, 0.667 and 2. The Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$ sample (the intermediate Cs-content commonly found in the literature) displayed similar results for the majority phase. However, in the minority phase, the ratios of Ba, Cs, and Ga varied greatly between samples. The stoichiometry of Ga reached 3.63 and 3.98 in Ba$_{0.667}$Cs$_{0.667}$Ga$_2$Ti$_6$O$_{16}$ and Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$, which are much higher than the majority phase Ga content. In addition, according to charge balance considerations, the amount of Cs at A sites in the minority phase must be greater than that in the majority. Thus, the Cs concentration at A sites of the minority phase was 20% and 118% higher than the target phase in Ba$_{0.667}$Cs$_{0.667}$Ga$_2$Ti$_6$O$_{16}$ and Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$, respectively. In recent work, it was found that high Cs concentrations represent the most thermodynamically favorable state for these hollandite systems. In light of these findings, one potential explanation of the Ga-rich and Cs-rich phase detected by TXM, could be due to a thermodynamic driving force to form a more stable phase.

The analysis above indicates that the observed rod-like, Ga-rich regions may actually be different stoichiometries/composition of the primary hollandite phase. The heterogeneous nature of this single-phase hollandite could be expected in a solid-state ceramic processing route where a sample’s homogeneity is determined by physical mixing coupled with diffusion and (potentially incomplete) phase reaction processes at elevated temperature. This picture of the materials system could explain why only hollandite was detected by lab-based XRD (i.e., because the lattice parameters and changes between the majority and minority phases of the single hollandite phases were too small to detect), while “hot spots” in local Ga composition were detected by TXM and SEM-EDS.


Figure 4.8. The EDS point result of majority and minority phases are list in (a-c) Ba$_{0.667}$Cs$_{0.667}$Ga$_2$Ti$_6$O$_{16}$ and (d-f) Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Target Phase</th>
<th>Majority Phase</th>
<th>Minority Phase</th>
<th>Target Phase</th>
<th>Majority Phase</th>
<th>Minority Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.667</td>
<td>0.633</td>
<td>0.442</td>
<td>1.040</td>
<td>1.010</td>
<td>0.490</td>
</tr>
<tr>
<td>Cs</td>
<td>0.667</td>
<td>0.592</td>
<td>0.663</td>
<td>0.240</td>
<td>0.190</td>
<td>0.340</td>
</tr>
<tr>
<td>Ga</td>
<td>2.000</td>
<td>1.930</td>
<td>3.630</td>
<td>2.320</td>
<td>2.300</td>
<td>3.980</td>
</tr>
<tr>
<td>Ti</td>
<td>6.000</td>
<td>6.000</td>
<td>6.000</td>
<td>5.680</td>
<td>5.680</td>
<td>5.680</td>
</tr>
<tr>
<td>O</td>
<td>16.000</td>
<td>16.000</td>
<td>16.000</td>
<td>16.000</td>
<td>16.000</td>
<td>16.000</td>
</tr>
</tbody>
</table>

Table 4.1. The chemical composition of Ba$_{0.667}$Cs$_{0.667}$Ga$_2$Ti$_6$O$_{16}$ and Ba$_{1.04}$Cs$_{0.24}$Ga$_{2.32}$Ti$_{5.68}$O$_{16}$.

Using each estimated stoichiometry for the majority and minority hollandite phases, their transmission properties were estimated using the CXRO x-ray calculator and the estimates were compared against the contrast observed in the TXM images. Figure 4.9 shows the absorption edges calculated for the minority (red), majority (green), and target (blue) hollandite phases. The plots suggest three expectations for the contrast above and below the Ga k-edge: (1) Below the edge, the minority phase absorbs less (and transmits more) than the majority phase and, therefore, should appear darker in the below-edge images (TXM images are presented in “reverse contrast”); (2) Above the edge, the minority phase absorbs more and should appear lighter than the majority phase; and (3) Across the edge, the minority phase’s change in contrast should be greater than that of the majority phase (a 7% change in the majority phase versus a 22% change in the minority for the high cesium composition and a 16 versus a 33% change for the lower cesium composition). If the contrast measured in the TXM images is consistent with the three expectations listed above, then the TXM results support the SEM-EDS analysis of the majority and minority hollandite phases.

Figure 4.9. Calculated Ga x-ray absorption k-edges for minority, majority, and target hollandite phases in the intermediate and higher Cs-content single-phase hollandite systems.
The TXM images are in fact consistent with all three of the expectations. For both the literature Cs and high-Cs samples, the minority hollandite phase appears darker in the below-edge image and lighter in the above-edge. Furthermore, the percent changes in contrast for both samples are consistent with those predicted. The minority phase’s contrast changed by 27% and 29% in the literature and high-Cs content samples, respectively. The corresponding predicted changes were 33% and 22%. The contrast changes exhibited by the majority phase in the literature and high-Cs content samples were 13% and 12%, respectively, where the corresponding predicted values were 16% and 7%. Exact agreement between the predicted and measured values was not expected because the CXRO calculator does not take into account porosity. Therefore, the TXM results are very much consistent with the SEM-EDS analysis that suggested the presence of a majority and minority composition of the same single-phase hollandite.

4.2.3 Sintering Studies of Hollandite and pyrochlore Nd$_2$Ti$_2$O$_7$ dual phase ceramic

A baseline hollandite with the composition Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ was chosen for this study along with Nd$_2$Ti$_2$O$_7$. Previous calculations displayed in Table 5.1 have indicated that mixtures of the hollandite + Nd pyrochlore are required to be near the ratio of 50 vol% hollandite and 50 vol% Nd-pyrochlore in order access the required 5% transmission change across the absorption edges of Ga and Nd. In order to explore these initial estimates, samples were made with i) 45/55, ii) 50/50 and iii) 55/45 vol% ratio of hollandite to pyrochlore respectively. In addition, in order to evaluate the ability of the instrumental technique to determine the presence of voids in the material, both porous (75% relative porosity) and dense (~95% relative density) samples were prepared. Sintering parameters for obtaining the target relative density were obtained by constructing Master Sintering Curves (MSC).$^{24}$

In order to obtain the MSCs of Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$, Nd$_2$Ti$_2$O$_7$ and dual phase materials, uniaxially pressed pellets of each composition were sintered at different heating rates (2, 5, 8 and 10°C min$^{-1}$) and the shrinkage was measured as a function of time.$^{25,26}$

The linear shrinkage rate using densification by both volume and grain boundary diffusion mechanism is given by equation (3):$^{24}$

$$\frac{dL}{Ldt} = \frac{\gamma \Omega}{kT} \left( \frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4} \right)$$  \hspace{1cm} (3)

Where, $L =$length of the sample (m)

t= time (sec)

$\gamma = $ surface energy (J/m$^2$)

$\Omega =$atomic volume (m$^3$)
k=Boltzmann constant ($1.38066 \times 10^{-23} \text{ J/K}$)

$T$= absolute temperature (K)

$G$=mean grain diameter (m)

$D$=diffusion coefficient ($\text{m}^2/\text{sec}$)

$\delta$=width of grain boundary (m)

$\Gamma$=scaling factors representing the relative contributions of volume and grain boundary diffusion

$Q_a$= activation energy

Subscript, v= volume, b=grain boundary

Using a separation of variables described in Reference$^{24}$, with the assumption that there is a single dominant diffusion mechanism and the density is uniform, Equation (3) can be written as the generalized MSC equation displayed in equation (4):

$$\theta(t, T(t)) \equiv \int_0^t \frac{1}{T} \exp \left( \frac{Q_a}{RT} \right) dt$$

(4)

After simplification, equation (5) is used to calculate the density contour maps using the following relationship,$^{25,26}$

$$\rho = \rho_o + \frac{a}{\left[1 + \exp\left(-\frac{\log(\Theta_o) - \log(\Theta)}{b}\right)\right]^c}$$

(5)

where $\log(\Theta_o)$ and the factors a,b,c are obtained by fitting the experimental density curves at different heating rates to the MSC and $\rho_o$ is the green density.

Figure 4.10 shows the density contour maps for Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ and Nd$_2$Ti$_2$O$_7$. It was found that the highest temperature for Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ to arrive 100% density was 1300 $^\circ$C while it was 1500 $^\circ$C for Nd$_2$Ti$_2$O$_7$. The value of these maps is that they prescribe the thermal treatment needed to achieve a particular density.
Figure 4.10. Contour map showing the prediction of the sintering time for a: \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \) and b: \( \text{Nd}_2\text{Ti}_2\text{O}_7 \).

Figure 4.11 gives the density contour map of \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \) and \( \text{Nd}_2\text{Ti}_2\text{O}_7 \) dual phase at the volume fraction of 50:50. For this dual phase sample, the density could reach 70% at the heating rate of 3 °C min\(^{-1}\) up to 1250 °C and holding at this temperature for a duration of 2 hours. In order to achieve a relative density of 95%, one possible heat treatment is heating rate of 3 °C min\(^{-1}\) up to 1300 °C and holding at this temperature for a duration of 10 minutes. The conditions derived from the density contour maps were used to prepare the model two-phase samples with the desired density. The microstructure of these sintered samples is shown in Figure 4.12 and 4.13.

Figure 4.11. Contour map showing the prediction of the sintering time for \( \text{Ba}_{1.33}\text{Ga}_{2.66}\text{Ti}_{5.34}\text{O}_{16} \) and \( \text{Nd}_2\text{Ti}_2\text{O}_7 \) dual phase at the volume fraction of 50:50.
Figure 4.12. Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ and Nd$_2$Ti$_2$O$_7$ composite samples with a) 45/55, b) 50/50 and c) 55/45 volume fraction hollandite/pyrochlore sintered at 1300°C for 2h with relative density of 95%.

Figure 4.13. Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ and Nd$_2$Ti$_2$O$_7$ composite samples with a) 45/55, b) 50/50 and c) 55/45 volume fraction hollandite/pyrochlore sintered at 1250°C for 10 min with relative density of 70%.
4.2.4 3D Structure of Model Dual Phase Ceramic Waste Forms

Differential X-ray absorption contrast tomography was performed on a total of eight samples in this study. Four of these samples were used to establish baseline measurements and are used as a means to evaluate the accuracy of the technique with respect to the CXRO predictions. These four samples consist of solely one model waste form material, namely two contain only Ba$_{1.33}$-hollandite, and the remaining two contain only Nd$_2$Ti$_2$O$_7$. The analysis of these model waste form materials is necessary for two reasons. As stated previously, it is possible to analyze these pure samples and compare the results to the predictions made by the CXRO calculator. This comparison establishes whether differential X-ray absorption contrast tomography is applicable to these material systems. The second reason is that these samples establish a basis for comparison when analyzing the more complicated samples consisting of a mix of Nd$_2$Ti$_2$O$_7$ and Ba$_{1.33}$-hollandite.

Table 4.2: Average volume fraction (%) for each phase in the Ba$_{1.33}$-hollandite baseline samples.

<table>
<thead>
<tr>
<th>Hollandite Baseline</th>
<th>Pore</th>
<th>Ga</th>
<th>Ga-Rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Fraction (%)</td>
<td>2.2</td>
<td>91.5</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Using image processing and segmentation techniques, the composition of the baseline samples were analyzed and the results for the Ba$_{1.33}$-hollandite samples are presented in table 4.2. Two solid phases were clearly identified based on their contrast change across the Ga k-edge. The primary solid Ga phase exhibited a lower contrast change as detailed in table 4.3, whereas the minority, Ga-Rich phase had a much higher contrast change. This is indicative of a much higher concentration of Ga in the minority phase.

Table 4.3: The XNT numerical results for the Ba$_{1.33}$-hollandite baseline sample. Values listed below are the average transmission contrast change (%) for each specific phase identified in table 4.2.

<table>
<thead>
<tr>
<th>Ba$<em>{1.33}$Ga$</em>{2.66}$Ti$<em>{5.34}$O$</em>{16}$</th>
<th>Bulk Ga</th>
<th>Ga-Rich</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Change (%)</td>
<td>2.7</td>
<td>11.9</td>
<td>0</td>
</tr>
<tr>
<td>CXRO % Change</td>
<td>13</td>
<td>13</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 4.3 lists the voxel statistics for the Ba$_{1.33}$-hollandite baseline sample. Upon inspection, it is clear that there are two distinct solid phases within the sample, labeled as regions “Bulk Ga” and “Ga-Rich”. “Bulk Ga”, which has a percent transmission change of 2.7% falls well below the CXRO predicted transmission percent change of 13%. The Ga-Rich region’s transmission percent change of 11.9 agrees with the CXRO prediction.
Table 4.4: Average volume fraction (%) for each phase identified in the pyrochlore baseline samples.

<table>
<thead>
<tr>
<th>Pyrochlore Baseline</th>
<th>Pore</th>
<th>Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Fraction (%)</td>
<td>8.3</td>
<td>91.7</td>
</tr>
</tbody>
</table>

Table 4.4 displays the composition of the pyrochlore baseline samples (% volume fraction) as obtained using image processing and segmentation techniques. A single solid phase was identified, labeled “Nd” and consists of the majority of the sample. This phase exhibits a contrast change consistent with the CXRO predictions and is detailed in table 4.5.

Table 4.5: The XNT numerical results for the Nd$_2$Ti$_2$O$_7$ baseline sample. Values listed below are the average transmission intensity values for each specific phase identified in Figure 4.7.

<table>
<thead>
<tr>
<th>Nd$_2$Ti$_2$O$_7$</th>
<th>Nd</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Change (%)</td>
<td>12.7</td>
<td>0</td>
</tr>
<tr>
<td>CXRO % Change</td>
<td>12</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 4.5 lists the voxel statistics of the single phase Nd$_2$Ti$_2$O$_7$ baseline material. These statistics were obtained by manually identifying regions within reconstructed sample cross sections at varying depths throughout the sample and measuring the average voxel intensity value. From the table, it can be seen that there are two distinct regions identified, namely a “Nd” containing region, and the background (or pore) region. “Nd” shows a percent change of around 12%, which agrees very closely with what is predicted by the CXRO calculator (listed in the “CXRO Change” column).

Mixing Samples

The remaining four samples that have been analyzed consist of a 50:50 Nd$_2$Ti$_2$O$_7$:Ba$_{1.33}$-hollandite composition. In addition to changing the composition, the porosity of the samples was also varied. Of these four samples, two were fabricated to be 30% porous (70% dense), the remaining two, 5% porous (95% dense).

Table 4.6 below shows the results from the differential X-ray absorption contrast tomography. Three distinct phases were identified. Namely a phase containing Nd, and two phases containing Ga have been identified. These results are consistent with the analysis of the baseline samples, where a singular Nd phase was identified in the Nd$_2$Ti$_2$O$_7$ sample, and two distinct phases, one bulk, low Ga content phase, and one Ga rich phase in the Ba$_{1.33}$-hollandite sample.
Table 4.6: Average volume fractions (%) for each phase present in the 5 % porous and 30 % porous mixed samples

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pore</th>
<th>Nd</th>
<th>Ga</th>
<th>Ga-Rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % Porous</td>
<td>5.2</td>
<td>42</td>
<td>51.4</td>
<td>1.4</td>
</tr>
<tr>
<td>70 % Porous</td>
<td>34.5</td>
<td>23.6</td>
<td>41.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4.2.5 Advanced Characterization of Model Dual Phase Ceramics

Figure 4.14 displays the Backscattered Electron Image (BSE) of Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ and Nd$_2$Ti$_2$O$_7$ dual phase sample polished surface. The Energy Dispersive Spectroscopy (EDS) mapping displays the element distribution of Ba, Nd, Ti and Ga.

![BSE image of Ba$_{1.33}$Ga$_{2.66}$Ti$_{5.34}$O$_{16}$ and Nd$_2$Ti$_2$O$_7$ dual phase sample polished surface area and EDS mapping for element Ba, Nd, Ti and Ga.](image)

In previous studies, two distinct morphologies have been identified within Ga-containing materials. The primary structure which occurred in the Ga-rich region is globular in nature. A secondary cylindrical structure was identified in the interior of samples which also contained Cs. As none of the samples analyzed in this study contained Cs, it is expected that these rod-like structures would not occur, and that the Ga-rich regions should only exhibit a globular morphology.

Additional 3-D morphological studies on these model systems were performed using FIB-SEM techniques to provide a basis of comparison to the XNT studies summarized above. Circular fiducial markers were milled into the samples and, during the automated data collection, were used to align the area of interest during subsequent milling and BSE mapping steps. It is
important that the sample be well-aligned so that the amount of materials milled away in each step is consistent and controlled, as shown in Figure 4.15. Alignment is also important to ensure that the BSE maps are being collected from the same region in subsequent steps. Figure 4.15 shows the BSE image of a sample electrode after appropriate sample preparation.

A section of approximately $10 \times 10 \times 10 \, \mu m$ was removed from the bulk electrode and a ex-situ slice and view technique was applied to obtain a sequence of 214 images. The volume fractions of each phase and their corresponding grain size distribution across the volume were determined using the procedure outlined in Ref\textsuperscript{13}. Figure 4.15 a, b and c depict the 3D structure of the phases identified as a) $Ba_{1.33}Ga_{2.66}Ti_{5.34}O_{16}$, b) $Nd_2Ti_2O_7$, and c) $Ba$-$Nd$-$Ti$-$O$ phase. The calculated 3D structure was presented in Figure 4.16.

**Figure 4.15.** The BSE images for ion beam milled $Ba_{1.33}Ga_{2.66}Ti_{5.34}O_{16}$-$Nd_2Ti_2O_7$ dual phase sample in different layers.
4.2.6 Multi-scale Modeling

Surface-based and volume-based investigations are directly coupled, and are parts of the total problem of understanding and designing heterogeneous waste form materials for maximum functional storage and long term safety (minimum loss of stored materials over their lifetime). Figure 4.17 illustrates that relationship conceptually. Based on estimates of the rate controlling processes during waste form service, we postulate that the flux of stored material out of the waste form in a generalized service environment is dominated in the early stages of life by direct leaching of surface materials, assisted by concentration gradient driven flux in the bulk region near the surface, as suggested schematically in Fig. 4.17. We further postulate that the “end of life” of the storage material is defined by a sharp acceleration of the elemental flux rate when the distributed void regions in the bulk created by the diffusive mass loss create a “critical path” which couples the interior to the surface, possibly involving grain boundary (or other) corrosive pathways created by the surface leaching. When that occurs, the rate of release and corrosive attack is greatly enhanced, and physical degradation of the waste form (including it’s mechanical strength) is rapid and accelerating. Discussion of the onset of that accelerated behavior and waste form failure is not attempted in the present program, but the present milestone attempts to provide the bulk diffusion foundation stones of this degradation and the functional failure.

Figure 4.16. The 3D structure of (a) Ba1.33Ga2.66Ti5.34O16, (b) Nd2Ti2O7 phase, (c) Ba-Nd-Ti-O, and (d) the spatial distribution of each phase in bulk. The structure is derived from in-situ FIB-SEM images.
concept for heterogeneous materials to enable the creation of the complete model, and to provide a mechanistic model that is set on the as-designed and as-manufactured heterogeneous morphology. The present report focuses on the milestone of completing the Multiphysics conformal flux model based on observed microstructure of as-manufactured materials in Stage II of the process outlined in Fig. 4.17.

Figure 4.17. Relationship of surface to volume diffusive release mechanisms in heterogeneous waste form materials.

For the examples shown in this report, the heterogeneous waste form with composition $\text{Ba}_{0.667}\text{Cs}_{0.667}\text{Ga}_2\text{Ti}_6\text{O}_{16}$ with high cesium content was modeled, supported by the unique material constituent and morphology characterization capabilities of other team members that provided us with 3-D renderings of the as-manufactured morphologies as a starting point. We have previously published examples of finite element flux analysis of similar systems for ion transport membranes representing real 3D microstructure domains provided by Chiu et al. The sample shown here had a chemical composition $\text{Ba}_{1.04}\text{Cs}_{0.24}\text{Ga}_2.32\text{Ti}_{5.68}\text{O}_{16}$. X-ray nano-tomography was used to generate 3D representations of the waste forms by using the X-ray absorption behavior of the constituents. Each point in the tomography data represents different materials based on their intensity. Segmentation of the 3D tomography to different phases, generation of a computational domain for each phase and mesh generation for the domains for the finite element analysis was
performed by using the Simpleware™ code. Figure 4.18 shows a Simpleware generated finite element mesh from tomography data. The rendering method is illustrated by the schematic drawing in Fig. 4.19.

**Figure 4.18:** 3D finite element mesh used for conformal computations.

**Figure 4.19:** Schematic of the conformal modeling approach used to capture the effect of microstructure on the flux of individual constituents in a waste form analysis for the determination of species flux and critical path formation as an indication of functional or mechanical failure.
Figure 4.20 shows three phases of the waste form material, the Hollandite matrix, and a secondary emergent phase containing high concentrations of Cs, and voids, rendered in Simpleware.

![Figure 4.20: Three phases in the hollandite waste form a) void phase, b) Cesium rich secondary emergent phase and c) Solid Hollandite matrix.](image)

Due to the large number of mesh elements required to solve the static problem, we used an iterative solver to obtain the solution. In this model, we assumed that at the initial condition, the waste form would have higher concentrations of Cesium in the interior of the Hollandite and secondary phases. The outside boundary was specified to have a very low Cs concentration during the simulation. This created a chemical potential gradient of Cs between the interior and outside boundary which drove the flux according to equation (1) outlined in the methods section.
Figure 4.21: Calculated flux paths of Cs ions from the bulk center toward the boundaries through a Hollandite waste form structure.\(^{28}\)

Figure 4.21 shows a representation of the Cesium flow paths through the example structure. The flow of ions through the material is determined by the initial chemical potential present due to the variation of concentration of Cs between interior and external boundaries and flows toward the lower concentration regions. It is clear that these “critical paths” through the actual microstructure are determined by the morphological details and by the vector gradients of the concentration in various directions, as well as by the details of the diffusion properties of the individual phases, and that the occurrence of these critical paths determines the function and effectiveness of the heterogeneous waste form material.\(^{28,29}\)

In order to identify the important parameters in the general problem and to set some rules for the design of such heterogeneous material forms, we conducted a companion study of various parameters associated with the analysis demonstrated above. These studies were conducted with various model material arrangements to isolate the controlling parameters and behavior characteristics, as a function of how the materials are designed and assembled. For that situation, our representative volume element (in 2-D) is shown in Fig. 4.22, for which all interior boundary surfaces are specified with zero-flux boundary conditions to ensure that there is identical behavior in all interior directions, and one “free” boundary surface is defined to represent the external ambient region.
The general nature of the present problem and the uniqueness of the behavior we are modeling are illustrated by the calculated flux of waste material out of the stored phase (just one particle in this example) with increasing time, illustrated in Fig. 4.22. As we noted in Fig. 4.17, although we do not address the details of the external surface (or storage overburden) effects in this report, the present analysis is constructed such that those details can be subsequently modeled and coupled / combined with the current model. However, the unique nature of this problem is at the heart of the present model. Especially, how can we design the best heterogeneous material that will capture and hold a waste material for very long periods of time in a finite waste containment volume?

With the present mechanistic approach, the general nature of the problem can be understood, as shown in Fig. 4.23 and 4.24. In early life, diffusive flux out of the storage phase particles is randomly oriented in direction and local particles do not “see” the global low-concentration “free” surface unless they are very close to that boundary. As time passes, e.g. day 10, the flow of the flux is clearly directed away from the high concentration particle(s) and along the (radial) directions of decreasing concentration. By day 100 and 1000 the flux is clearly flowing along concentration gradient directions that are defined by the boundaries of the local constraints (which would generally include other particles as in Fig. 4.24) and the “free” boundary; the flux lines (which must point down the concentration gradient at all points) are clearly curved lines and eventually point to the low concentration “free” surface of exit. Finally, at very long times, the influence of the specific details of the geometry and morphology of the storage particles is not seen, and the general concentration gradient from the interior to the surface must become a linear slope. Depending on the details of the concentrations in the storage materials, their phase shapes, the morphology of the surrounding materials, and especially the diffusion coefficients of the phases of material in the heterogeneous waste material, the actual time scale of these events may be days, years, or eons. This is clearly an opportunity for design of the details of the material for optimum performance.
**Figure 4.23:** Flux flow directions and flow lines for increasing time after deployment of a two-phase heterogeneous waste form with one storage particle.

**Figure 4.24:** Flux flow directions and flow lines for increasing time after deployment of a two-phase heterogeneous waste form with several lenticular particles.
5 CONCLUSIONS

- Synchrotron-based transmission x-ray microscopy was used to image the 3-D microstructure of multiple phases within model waste form material systems. It was found that Ga doping levels consistent with those commonly used for nuclear waste immobilization (Ba\textsubscript{1.04}Cs\textsubscript{0.24}Ga\textsubscript{2.32}Ti\textsubscript{5.68}O\textsubscript{16}) could be readily imaged in single phase materials and hollandite/TiO\textsubscript{2} mixtures.

- SEM-EDS confirmed the chemical composition of a majority phase and a minority phase in the Ga-doped hollandite waste form material. Three-dimensional absorption contrast TXM images of the samples exhibited contrast changes across the Ga k-edge consistent with the SEM-EDS findings. The analysis suggests that the minority phase is a different stoichiometry/composition of the primary hollandite phase formed by the solid-state ceramic processing route.

- 3D spatial distributions of model waste form system containing two constituent phases. Ga–doped Ba hollandite (Ba\textsubscript{1.33}Ga\textsubscript{2.66}Ti\textsubscript{4.34}O\textsubscript{16}), and pyrochlore (Nd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}) of hollandite and pyrochlore were readily identified through the distributions Ga and Nd respectively.

- Synchrotron based TXM techniques were benchmarked with FIB-SEM serial section 3D renderings of model waste form material mixtures consisting of hollandite (Ba\textsubscript{1.33}Ga\textsubscript{2.66}Ti\textsubscript{4.34}O\textsubscript{16}), and pyrochlore (Nd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}) mixtures.

- We have developed a conformal multifunctional analysis method based on the Nernst Plank equation and postulated the method as a foundation for analysis-based design of heterogeneous waste form materials. The model describes charged species transport through different media by convection, diffusion, or migration, and the transport can be driven by chemical/electrical potentials or velocity fields. The model calculates species flux in the waste form with different diffusion co-efficient for each species in each constituent phase.

- We have found that “critical paths” of flux through the actual microstructure develop and are determined by the morphological details and by the vector gradients of the concentration in various directions, as well as by the details of the diffusion properties of the individual phases, and that the occurrence of these critical paths determines the function and effectiveness of the heterogeneous waste form material, and likely determine the life of those materials.

- Depending on the details of the concentrations in the storage materials, their phase shapes, the morphology of the surrounding materials, and especially the diffusion coefficients of the phases of material in the heterogeneous waste material, the actual time scale of these events may be days, years, or eons. This is clearly an opportunity for design of the details of the material for optimum performance and maximum safety for specified waste materials and conditions, and for a “design for life” approach to containment.
6 NEUP PUBLICATION AND PRESENTATION LIST

Publications


Paper in Preparation:


Presentations


9. K. Reifsnider, “Multiphysics Analysis of Aging in Heterogeneous Material Systems” Intern. Conf. of Computational and Experimental Engineering and Sciences Conference in on the occasion of the celebration of the Lifetime Achievement Award Medal to Dr. Jeffrey Fong, Changwon, Korea, June 2014 (Invited)


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