



# Crystallization behavior during melt-processing of ceramic waste forms



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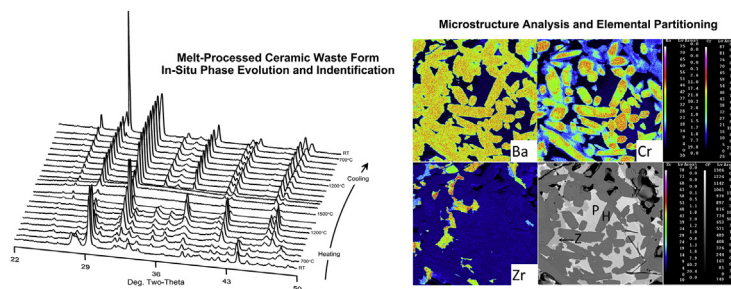
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## HIGHLIGHTS

- Crystallization behavior during **melt processing** multiphase ceramics was studied.
- Phase evolution order upon cooling was hollandite → perovskite → zirconolite → TiO<sub>2</sub>.
- Hollandite phases co-exists with a liquid phase at temperatures >1500 °C.
- Zirconolite crystallization is complex and involves intermediate phases.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Multiphase ceramic waste forms based on natural mineral analogs are of great interest for their high chemical durability, radiation resistance, and thermodynamic stability. Melt-processed ceramic waste forms that leverage existing melter technologies will broaden the available disposal options for high-level nuclear waste. This work reports on the crystallization behavior in selected melt-processed ceramics for waste immobilization. The phase assemblage and evolution of hollandite, zirconolite, pyrochlore, and perovskite type structures during melt processing were studied using thermal analysis, x-ray diffraction, and electron microscopy. Samples prepared by melting followed by annealing and quenching were analyzed to determine and measure the progression of the phase assemblage. Samples were melted at 1500 °C and heat-treated at crystallization temperatures of 1285 °C and 1325 °C corresponding to exothermic events identified from differential scanning calorimetry measurements. Results indicate that the selected multiphase composition partially melts at 1500 °C with hollandite coexisting as crystalline phase. Perovskite and zirconolite phases crystallized from the residual melt at temperatures below 1350 °C. Depending on their respective thermal histories, different quenched samples were found to have different phase assemblages including phases such as perovskite, zirconolite and TiO<sub>2</sub>.

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## 1. Introduction

Multiphase ceramic materials are of interest as an alternative to conventional borosilicate glass nuclear waste forms. Designing waste forms with the desired properties, including chemical corrosion resistance, radiation resistance, thermodynamic stability,

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and maximized waste loading, has been challenging [1]. Reprocessing used nuclear fuel (UNF) results in high-level waste (HLW) containing non-radioactive and radioactive elements that pose a long-term threat to the biosphere [2]. The idea of developing a suitable waste form for the various elements in a UNF HLW stream based on mineralogy is substantiated by the long-term durability of existing natural minerals [3,4].

Synroc, a titanate based multiphase material, has been proposed [5,6] to immobilize elements from nuclear waste streams. Synroc-C, a variant of Synroc formulation with hollandite, perovskite, zirconolite, and pyrochlore as major phases, is being developed for immobilizing HLW. Hollandite, with the general formula,  $[\text{Ba}_x\text{Cs}_y][\text{M}^{3+}_{2x+y}\text{Ti}_{8-2x-y}\text{O}_{16}]$  [7], is the primary host for Cs. The structure consists of a continuous network of edge and corner shared oxygen octahedra forming large tunnels running parallel to the *c*-axis [8,9].  $\text{Ti}^{4+}$  and  $\text{M}^{3+}$  reside in the oxygen octahedral while the heavier ions  $\text{Ba}^{2+}$  and  $\text{Cs}^+$  occupy the tunnel sites. Partial substitution of  $\text{Ti}^{4+}$  with trivalent cations  $\text{M}^{3+}$  or  $\text{Ti}^{3+}$  distorts the tunnel structure and facilitates the incorporation of larger Cs ions [10]. Perovskite ( $\text{CaTiO}_3$ ) predominantly hosts alkaline earth or rare-earth elements (REEs) as  $\text{Ca}^{2+}$  or  $\text{Ti}^{4+}$  can be easily substituted by REEs. Wide ranges of cation combinations are possible that preserve the perovskite structure (e.g.  $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ ,  $\text{A}^{3+}\text{B}^{3+}\text{O}_3$  and  $\text{A}^{1+}\text{B}^{5+}\text{O}_3$ ) [11]. Zirconolite ( $\text{CaZrTi}_2\text{O}_7$ ) or pyrochlore, with the general formula  $\text{A}_2\text{B}_2\text{O}_7$  ( $\text{A}^{3+}/\text{B}^{4+}$  or  $\text{A}^{2+}/\text{B}^{5+}$ ), is the preferred host for Zr and minor actinides [12]. Various processes including conventional sintering [13], hot isostatic pressing (HIP) [14], cold crucible induction melting (CCIM) [15], and spark plasma sintering [16] have been used to prepare these ceramic waste forms.

The present study supports ongoing work to develop melt-processing as a viable method to produce durable ceramic waste forms. The compositional dependencies of processing temperature and crystallization phenomena present challenges to melting and solidification of multiphase, multicomponent ceramic waste forms. The resultant microstructures and phase assemblage depend on several parameters such as composition, interaction between different components in liquid and solid states, mobilities and diffusivities of different constituents, crucible dimensions, heat transfer, etc. However, limited literature is available on the crystallization behavior in melt-processed ceramic waste form materials.

In this work, thermal analysis and quench studies were performed to better understand nucleation and crystallization sequences of phases during melt-processing of multiphase waste forms. The present findings provide insight and understanding of the crystallization phenomenon and its impact on microstructure evolution during melt-processing.

## 2. Experimental

### 2.1. Waste form composition and preparation

Savannah River National Laboratory (SRNL) developed the multiphase waste form composition [17–19] and provided batch materials for the experiments. The multiphase composition is based on simulated waste stream compositions that are currently being investigated under the DOE Fuel Cycle Research and Development (FCR&D) program. Stoichiometric amounts of reagent-grade oxides and carbonates were blended together, mixed in deionized water with zirconia media, and dried at 90 °C. The resulting material was used as feed stock for experiments. The target composition, designated CAF-MP, is listed in Table 1. Bulk melt-processing was performed by heating the feed material in an alumina crucible or Pt foil to 1500 °C at a rate of 5 K/min. Samples were typically held at 1500 °C for 20 min and cooled to room temperature at 5 K/min.

### 2.2. Viscosity measurements

Viscosity, as a function of temperature, was measured in accordance with the American International C965 Procedure A [20] in which the viscosity was measured using a rotating spindle and a fixed crucible (both constructed of Pt–20%Rh alloy). A portion of melt-processed (see Section 2.1) material was placed in the crucible and heated in a high temperature furnace. The temperature was initially set to achieve a condition (i.e. a melt or liquid–solid solution) in which the spindle could be lowered into the crucible. After steady-state conditions were obtained, the torque required to rotate the spindle at a constant speed was recorded with a Brookfield viscometer (Brookfield DV-II+, Brookfield Engineering Laboratories, USA). The temperature was then decreased incrementally and a series of such torque measurements at various temperatures was recorded until the viscosity increased beyond the instrument capability. Subsequently, a duplicate measurement was taken near the initial temperature to confirm the reversibility of the viscosity behavior. Experimentally derived instrument constants developed specifically for the SRNL system and verified with reference standards were used to calculate viscosity as a function of temperature from the recorded torque values [21,22].

### 2.3. Crystallization experiments

Differential scanning calorimetry (DSC) was used to investigate crystallization as a function of temperature. A SETSYS Evolution DSC instrument (SETARAM Inc., Hillsborough, NJ, USA) was used to measure the heat flow from the material during heating and cooling. Fig. 1 summarizes the DSC heating and cooling cycles. The maximum temperature for DSC measurements was 1500 °C, which was the melt-processing temperature used in this study. Heat cycles were chosen so that phase transformation behavior of CAF-MP, starting from unreacted stoichiometric mixture and as-formed compound, could be compared. A sample of 10–20 mg of starting material was heated under helium atmosphere in Pt crucibles. Two heating rates, 20 and 5 K/min, were used for this study.

Quenching experiments were performed to investigate endothermic and exothermic events identified in the DSC data. Approximately, 4–5 g of starting material was wrapped in a custom folded Pt foil and pinch sealed. These samples were heated to 1500 °C ( $T_m$ ), held for 20 min, cooled to temperature '*T*', equilibrated for time ' $t_{eq}$ ', and quenched in water by immersion. Temperature '*T*' corresponded to exothermic peaks identified in DSC data. Fig. 2 summarizes the time–temperature cycles used for these experiments.

### 2.4. Phase analysis

Quenched samples were crushed and characterized using x-ray diffraction (XRD) for phase identification (D2 Phaser, Bruker AXS, USA). Diffraction patterns were collected from powder samples over 10–70°  $2\theta$ , at a rate of 0.02° per second. Relative amounts of different phases were determined by quantitative analysis. For quantitative phase analysis, the TOPAS 4.2 (Bruker AXS, Karlsruhe, Germany) software package was used. Relative amounts of phases were determined by generating calculated XRD patterns using Rietveld quantitative phase analysis together with the PDF-4+ (2013) structural database for crystallographic information. To get the best-fit to the experimental pattern, appropriate Crystallographic Information Files (CIF) were taken from PDF-4+ database and Rietveld structural refinement of different corresponding phases was performed.

Quenched samples were also characterized using electron microscopy to complement the XRD results. Composition and phase

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