Crystallization Behavior during Melt-Processing of Ceramic Waste forms

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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_2 .

Keywords: waste form; crystallization; DSC; XRD, melt processing

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1.0 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, 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]. Ti^{4+} and M^{3+} reside in the oxygen octahedral while the heavier ions Ba^{2+} and Cs^+ occupy the tunnel sites. Partial substitution of Ti^{4+} with trivalent cations M^{3+} or Ti^{3+} distorts the tunnel structure and facilitates the incorporation of larger Cs ions [10]. Perovskite (CaTiO_3) predominantly hosts alkaline earth or rare-earth elements (REEs) as Ca^{2+} or Ti^{4+} can be easily substituted by REEs. Wide ranges of

cation combinations are possible that preserve the perovskite structure (e.g. $A^{2+}B^{4+}O_3$, $A^{3+}B^{3+}O_3$ and $A^{1+}B^{5+}O_3$) [11]. Zirconolite ($CaZrTi_2O_7$) or pyrochlore, with the general formula $A_2B_2O_7$ (A^{3+}/B^{4+} or A^{2+}/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.

2.0 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 de-ionized 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. Figure 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. This 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. Figure 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 $10 - 70^\circ 2\theta$, 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 assemblage was investigated using scanning electron microscopy (SEM) (FEI Quanta 200F, USA) equipped with a field emission gun. In general, multiphase areas from each sample were selected from back-scattered electron (BSE) images and elemental maps were collected using JEOL JXA-8200, WD/ED Combined Electron Probe Microanalyzer (EPMA) (JEOL Ltd., Tokyo, Japan). Elemental scans over the selected area were performed at an accelerating potential of 15kV, step size of $0.5\mu\text{m}$ in x - and y - directions, and a dwell time of 80 milliseconds at each point.

2.5 In-situ High-Temperature XRD studies

In-situ melting and solidification behavior of CAF-MP was studied using high-temperature XRD (HTXRD) measurements. In-situ HTXRD was carried out using a diffractometer (Siemens θ - θ D5000) equipped with a custom built high-temperature furnace using $\text{Co } K\alpha$

radiation. For the measurements, a thin, uniform layer of pre-reacted CAF-MP powder on a flat Pt disc was heated to 1500°C and cooled to room temperature. Diffraction patterns were collected at periodic isothermal temperature steps during the heating and cooling cycles, in the scan range 20-60° 2 θ , with step size 0.037° and a dwell time of 1s at each step.

3.0 Results and Discussion

3.1 Viscosity measurements

The behavior of the viscometer during the measurements was not consistent with a homogenous Newtonian liquid. The torque values increased and decreased sporadically and were accompanied by visible locking and slipping of the viscometer spindle. This effect was accentuated at lower temperatures. This is indicative of a crystal phase coexisting in equilibrium with the melt at high temperatures. The effect of crystallization on the measured viscosity is difficult to predict but, it is not equal to the true viscosity of the melt and depends on the crystallization process and the stoichiometry of the crystals [23]. However, once crystals impinge, the apparent viscosity will increase due to blocking or interlocking effects of these crystals and eventually, flow will cease as the sample becomes fully crystalline. Indeed, this type of behavior was observed and although the nature of the melt-crystal composition is unknown, the viscosity behavior appeared reversible in the time span of the measurement as evidenced by the data taken upon re-heating. Figure 3 shows viscosity (in Poise) versus 1/temperature (in K) for the CAF-MP composition. The plot shows a rapid increase in viscosity as a function of temperature at approximately 1480°C. It is unknown at what temperature the system is a complete melt because the liquidus temperature of the system was not determined.

3.2 DSC measurements and quenching experiments

Figure 4 shows DSC curves corresponding to 20 K/min and 5 K/min heating/cooling rates. Exothermic peaks between 1280 and 1330°C were consistently observed during cooling of raw material and pre-reacted material from the melt temperature. At higher cooling rates, a single broad peak was observed, as might be expected in case of rapidly cooled samples in which the DSC signal from individual phase evolution events was convoluted into a single event. The DSC results provide supporting evidence for the coexistence of crystalline phases with a melt in this system.

Quenching experiments were designed based on the exothermic peak temperatures from the DSC curves, believed to be related crystallization events. Varying heat treatment times (t_{eq}) were investigated to qualitatively understand phase evolution kinetics qualitatively. A baseline sample for comparison was heated to 1500°C, held for 4 h, and quenched. Table 2 summarizes the temperatures ' T ' and corresponding dwell times ' t_{eq} ' used for quenching experiments.

3.3 Phase analysis and microstructural characterization

All quenched samples, after heat treatment, were found to wet the Pt foil, indicating that melting occurred during their respective thermal histories. The baseline sample quenched from 1500°C was fully crystalline, as confirmed by XRD. Figure 5a compares the baseline measured XRD pattern to a calculated pattern using Rietveld quantitative phase analyses based on the following phases: TiO₂ (PDF: 04-006-3570), hollandite (PDF: 04-013-6380), and tazheranite (PDF: 04-008-0260). During XRD phase analyses, it was observed that many phases in the CaO-ZrO₂-TiO₂ system were close but not exact matches to the measured XRD patterns. Tazheranite ((Ca,Zr,Ti)O₂) is a naturally occurring cubic ZrO₂ where Zr⁴⁺ is partially substituted by Ca²⁺ and Ti⁴⁺ ions [24, 25]. Pure ZrO₂, naturally occurring as baddeleyite, has monoclinic symmetry but

transforms to tetragonal symmetry at 1170°C and to cubic symmetry at 2370°C [25]. Cubic ZrO₂ with a fluorite-type structure can be stabilized at lower temperatures by the addition of tetravalent cations [26], trivalent rare-earth oxides, or divalent cations like Ca²⁺ [27]. In addition to these, a number of other phases with similar structural motifs – calzirtite (Ca₂Zr₅Ti₂O₁₆), zirconolite (CaZrTi₂O₇), perovskite (CaTiO₃/CaZrO₃) – that are stable at temperatures greater than 1200°C have been reported [28, 29]. It can be understood that precise identification of zirconolite or related structures would become challenging during crystallization of multiphase melts given that a wide range of elements can form solid solutions with different phases in the CaO-ZrO₂-TiO₂ system. Therefore, the chemistry of each phase in the X-ray Rietveld analysis were defined where possible using the elemental analysis from microscopy. The peaks indexed as tazheranite (Figure 5a) could correspond to several phase(s) in the CaO-ZrO₂-TiO₂ system and hereafter referred to as Ca-Zr-Ti-O phase.

A representative microstructure of the sample quenched from 1500°C is shown in Figure 5b. In that image, the darkest gray phase corresponds to rutile (R), the mid-tone gray phase corresponds to hollandite (H) and is characterized by its large aspect ratio, and the brightest color phase corresponds to Ca-Zr-Ti-O (C). WDS elemental mapping images for selected elements are shown in Figure 6. The elemental maps show distinct partitioning of hollandite specific elements (Ba, Cr, and Cs) and a Ti rich phase that was presumably TiO₂. A distinct feature observed in the hollandite phase was a compositional gradient of Cr and Fe across the grains, as seen by comparing Cr and Fe elemental maps in Figure 6. This phenomenon was observed in samples heat treated at 1325 and 1285°C as well and is believed to be indicative of a fractional crystallization process as will be discussed later. Preferential partitioning of Nd, Zr, Ca, and Zr to the bright Ca-Zr-Ti-O phase was also observed in Figure 6.

The corresponding diffraction peaks in Figure 5a, as mentioned earlier, match with multiple structures such as cubic ZrO_2 , ZrTiO_4 , zirconolite, and others in the $\text{CaO-ZrO}_2\text{-TiO}_2$ system that can host any of the observed elements in their respective lattices.

Figure 7 summarizes the XRD and SEM results for the samples heat treated at 1325°C for 1 h, 12 h and 24 h. Figure 7a shows the quantitative Rietveld refinement results based on the following phases: TiO_2 (PDF: 04-006-3570), hollandite (PDF: 04-013-6380), tazheranite (PDF: 04-008-0260), perovskite (PDF: 04-014-7761), and zirconolite (PDF: 04-002-4312). The same phases (hollandite, rutile, and Ca-Zr-Ti-O) observed in the sample quenched directly from 1500°C were also observed in the sample annealed at 1325°C . In addition, a perovskite and a Zr-rich phase, separate from the Ca-Zr-Ti-O phase, were identified. The perovskite phase was found in all samples, whereas the Zr-rich phase, in samples annealed for long times (12 h and 24 h), as evidenced by the best fit to the experimental pattern when both tazheranite and zirconolite were assumed to be in the system. This suggests zirconolite is the Zr-rich phase evolving from Ca-Zr-Ti-O . However, the particular chemistry of these phases remains unknown.

BSE contrast images presented in Figure 7b support the XRD results and show at least 4 distinct phases in the sample annealed for 24 h. WDS mapping images of selected elements in this sample are shown in Figure 8. The mid-tone gray phase in Figure 7b was identified as hollandite (H) and was found to have the target chemistry (Ba, Cr, Fe, Ti and Cs) based on Figure 8. Importantly, Cs remained incorporated within the hollandite phase after annealing for 24 h, indicating thermal stability of the hollandite phase with respect to Cs retention. Rutile (R) is indicated as the darkest gray phase in Figure 7b. Two distinct phases, apart from hollandite and TiO_2 , could also be observed in the BSE image of the sample corresponding to $t_{\text{eq}} = 24$ h. WDS maps show that both these regions exhibited uniform Ti distribution, as would be expected

in both perovskite and zirconolite structures. Ca is present in both phases, but more concentrated in the brightest phase, which is also consistent with perovskite and zirconolite structures. This is further supported by the elemental map showing Nd-rich areas in the brightest phase. The light gray phase is rich in Zr and Ca, which is consistent with a zirconolite phase.

The XRD and SEM results indicate that perovskite and Zr-rich phases crystallize at lower temperatures than the primary hollandite phase. This is further supporting evidence for the coexistence of crystalline phases with a melt in this system, in agreement with viscosity and DSC data. A chart showing the percentage of each phase as a function of annealing time is shown in Figure 9. Significant differences in phase abundance were measured in samples annealed for 1 h compared to 12 h or 24 h indicating that at 1325°C, the kinetics of phase evolution and development was relatively slow by the order of hours.

Figure 10 summarizes the XRD and SEM results for the samples heat treated at 1285°C for 1 h, 12 h and 24 h. Figure 11 shows the elemental distribution in the sample treated for 24 h at 1285°C. Figure 10a compares the measured XRD patterns to calculated patterns using Rietveld quantitative phase analyses based on the following phases: TiO₂ (PDF: 04-006-3570), hollandite (PDF: 04-013-6380), tazheranite (PDF: 04-008-0260), perovskite (PDF: 04-014-7761), and zirconolite (PDF: 04-002-4312). XRD phase analysis and BSE images (Figures 10a and 10b) of different samples, annealed at 1285°C for different holding times and quenched, show similar phase assemblage and evolution as observed at 1325°C. Perovskite and Zr-rich phase were present in all samples that were annealed for varying times. The Zr-rich phase that was observed in the sample treated at 1325°C for longer times was seen at 1285°C even after 1 h. Figure 12 shows a chart of the percentage of each phase as a function of annealing time. Significant differences in phase abundance were measured in samples annealed for 1h compared

to 12 h or 24 h, indicating that at 1285°C, the kinetics of phase evolution and development was relatively slow as well.

Greater understanding of the crystallization behavior of melt processed synroc-based ceramics can be made by comparing the phase and microstructural analysis of samples heat treated at 1285, 1325, and 1500°C. With respect to phase evolution, the kinetics was time dependent at both temperatures but the type was not. For samples heat-treated at 1325°C, the hollandite phase concentration remained relatively constant over 24 h, whereas the perovskite and Ca-Zr-Ti-O concentrations increased over time. An opposite trend was observed in samples heat treated at 1285°C; the perovskite and Ca-Zr-Ti-O concentrations remained relatively constant over 24h, whereas the hollandite concentration increased with time. In both cases, the amount of TiO₂ relative to the primary phases (hollandite, perovskite, and Ca-Zr-Ti-O) was greater at shorter times (1 h) than longer times (24 h). TiO₂ was the primary constituent of all the phases in the system and it followed that available TiO₂ would be used up during crystal growth of all the primary phases. However, the concentration of TiO₂ with time was not consistent for both temperatures. Although TiO₂ concentration appeared to decrease with time for samples cooled to 1285°C, that trend was not observed for samples cooled to 1325°C.

Distinct compositional gradients of Cr and Fe across the phases associated with hollandite are visually apparent in the elemental maps in Figures 6, 8, and 11. High concentration of Fe along the edges of hollandite grains, accompanied by a decrease in Cr intensity towards the edges, can be seen. This phenomenon was more pronounced in samples quenched from lower temperatures (i.e. 1285°C > 1325°C > 1500°C). Collectively, these results could indicate different crystal growth temperature regimes for the different phases or crystallization sequences or

growth regimes that is dependent on other factors such as the composition of any residual melt or heterogeneous nucleation sources.

In general, the observed behavior resembles fractional crystallization such as reported during the solidification of zirconolite melts [30]. In that research, the crystallization sequence for zirconolite ($\text{CaZrTi}_2\text{O}_7$) was reportedly $\text{Ti-bearing ZrO}_2 \rightarrow \text{ZrTiO}_4 \rightarrow \text{Zr-rich CaZrTi}_2\text{O}_7 \rightarrow \text{Zr-poor CaZrTi}_2\text{O}_7$. The phases formed early at higher temperatures reportedly reacted with the residual melt to produce Zr- and Ti- rich phases surrounding each previously formed phase. The composition of the phases was correlated to the enrichment or depletion of Zr and Ti in the residual liquid phase expressed by peritectic/eutectic points in a pseudo-binary system [30]. Further explanation of the phase evolution behavior in the CAF-MP system is presented in section 3.4.

3.4 High-Temperature X-Ray Diffraction

Figures 13 and 14 show in-situ XRD patterns collected during heating and cooling of CAF-MP, respectively. A baseline diffraction pattern was taken at 25°C, before the start of the heating cycle, to confirm the phase composition of the starting material. As shown in Figure 13, the primary starting materials, (e.g. TiO_2 , BaCO_3 , ZrO_2 , Cs_2O_3 , etc.) were identified. Initial indications of reaction were observed in the 800°C XRD pattern, which could first be identified in the 900°C XRD patterns matching with hollandite and perovskite phases. The peak intensities associated with hollandite and perovskite phases were observed to grow with increasing temperature, accompanied by decreasing peak intensities of phases identified in the baseline pattern, indicating a solid-state reaction process. Initially, presence of a liquid (i.e., amorphous) phase was observed in the 1400°C XRD pattern as evidenced by an amorphous hump between 40 - 60° 2 θ and a decrease in the peak intensities of the perovskite phase from lower

temperatures. At 1500°C, the XRD patterns indicated an amorphous phase in combination with the hollandite phase and no indication of secondary crystalline phases. The XRD scans from 700°C to 1500°C confirm the initial reaction of the pre-cursor powders, the subsequent formation and in-growth of crystalline phases (i.e., hollandite and perovskite), and eventual partial melting of the system by dissolution of the all crystalline phases except the hollandite phase, which remains in combination with a liquid phase at temperatures up to at least 1500°C, the highest temperature studied.

The XRD pattern at 1500°C in Figure 13 is the baseline pattern for the subsequent cooling cycle. That pattern is reproduced again in Figure 14, in which hollandite and an amorphous (melt) phase are evident. Upon cooling, hollandite in-grew and remained the only crystalline phase as evidenced by the 1500 – 1400°C XRD patterns. Peaks identified as belonging to perovskite and Ca-Zr-Ti-O phases appeared in the 1350°C XRD pattern. No measureable amorphous phase was identified in the 1350°C XRD pattern indicating the crystalline phases that appeared at 1350°C precipitated from the liquid. A set of minor peaks was observed in the XRD patterns at temperatures less than 1350°C, which were attributed to TiO₂. This result indicates that TiO₂ identified in fully cooled samples precipitated upon cooling, which is known to exist in zirconolite systems [27]. Taken together, the HTXRD scans from 1500°C to 1100°C confirm that at 1500°C the system consisted of a partial melt with a hollandite phase, and that upon cooling, hollandite continued to in-grow followed by the eventual formation of perovskite and Ca-Zr-Ti-O phases, accompanied by disappearance of the liquid phase at ~1350°C. Minor amounts of TiO₂ precipitated at ~ 1300°C and further cooling did not result in significant phase evolution observable to the XRD patterns, indicating complete crystallization.

Phase evolution behavior identified from HTXRD further supports our understanding of the trend of relative phase amounts showed in Figures 9 and 12. At 1325°C after 1 h, the sample quenched was crystallized to be predominantly hollandite and the other phases being perovskite, Ca-Zr-Ti-O and TiO₂. The relatively high amount of TiO₂ observed in the sample quenched from 1285°C after 1 h (compared to 1325°C after 1 h) can be attributed to the precipitation of TiO₂ at lower temperatures of ~1300°C. Upon annealing, the system progressed towards equilibrium resulting in relative growth or reduction of different phases as discussed in Section 3.3.

4.0 Conclusions

It has been demonstrated that the multiphase ceramic system is not a homogeneous melt at 1500°C but instead consists of nominally stoichiometric hollandite with a melt comprised of the remaining constituents. As the material is cooled, a Zr-rich phase that evolves into zirconolite and a mixed Ca-lanthanide series perovskite phase begin to form. TiO₂ is also observed to ingrow upon further cooling. XRD and microstructural analysis of quenched samples suggest that the identified DSC peaks correspond to crystallization of perovskite (~1325°C) and zirconolite (~1285°C). Both zirconolite and perovskite phases are observed in samples quenched from either 1285 and 1325°C after holding for >12 h. However, zirconolite is not observed in the sample quenched from 1325°C after 1 h, suggesting perovskite precedes zirconolite crystallization upon cooling. In summary, the data indicates the order of phase evolution upon cooling in this system is hollandite → perovskite → zirconolite → TiO₂. A wide range of substitutions is possible and expected in both phases and was observed in the WDS maps. Parasitic phases incorporating other elements have not been identified. An observed partitioning of Cr and Fe species within the hollandite phase has to be further examined.

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Table Captions

Table 1. Target composition of CAF-MP

Table 2. Temperature parameters used for quenching experiments

Figure captions

Figure 1. Temperature-time profile used for DSC experiments. ' α ' is the constant heating/cooling rate used.

Figure 2. Heat cycle used for quenching experiments.

Figure 3. Viscosity as a function of temperature for CAF-MP. The accuracy of individual viscosity values is +/- 20% based on historical data for a reference material measured on the same instrument. The lines through the data are linear fits to aid the eye.

Figure 4. DSC curves showing exothermic peaks between 1280°C and 1330°C. The sharp peak on the dotted line (5 K/min) is an external fluctuation.

Figure 5. (a) Quantitative XRD analysis of CAF-MP quenched from 1500°C and held for 4 h. Best fit for Rietveld pattern refinement was obtained with hollandite (H), TiO₂ (T) and tazheranite (C) (b) Corresponding back-scattered images.

Figure 6. WDS maps of selected elements of CAF-MP at 1500°C annealed for 4 h. Different phases are labelled on the BSE graphic - hollandite (H) and TiO₂ (T). The brightest background phase is Ca-Zr-Ti-O.

Figure 7. (a) Quantitative XRD analysis of CAF-MP quenched from 1325°C held for varying times. Best fit for Rietveld pattern refinement was obtained with hollandite (H), TiO₂ (T), tazheranite (C) and zirconolite (Z) (b) Corresponding back-scattered images.

Figure 8. WDS maps of selected elements of CAF-MP at 1325°C annealed for 24h. Different phases are labelled on the BSE graphic. (Multiple sweeps were done across the selected area to collect the maps. A shift in the scanned area occurred between different sweeps, as seen in few elemental maps. No shift was observed during individual sweeps.)

Figure 9. Quantitative phase distribution as a function of annealing time at 1325°C. Ca-Zr-Ti-O represents both tazheranite and zirconolite phases from Rietveld refinement.

Figure 10. (a) Quantitative XRD analysis of CAF-MP quenched from 1285°C held for varying times. Best fit for Rietveld pattern refinement was obtained with hollandite (H), TiO₂ (T), tazheranite (C) and zirconolite (Z) (b) Corresponding back-scattered images.

Figure 11. WDS maps of selected elements of CAF-MP at 1285°C annealed for 24 h. Multiple sweeps were done across the selected area to collect the maps. (Here also, a shift in the scanned area occurred between different sweeps, as seen in few elemental maps.)

Figure 12. Quantitative phase distribution as a function of annealing time at 1285°C. Ca-Zr-Ti-O represents both tazheranite and zirconolite phases from Rietveld refinement.

Figure 13. In-situ XRD patterns collected at different temperatures during heating from 25°C to 1500°C. Different phases in the starting material are B-BaCO₃, Z-ZrO₂, T-TiO₂ (anatase), Cs-Cs₂CO₃, C-CeO₂, and Cr-Cr₂O₃.

Figure 14. In-situ XRD patterns collected during cooling from 1500°C to room temperature (RT).

Table 1.

	Target wt% of each oxide in CAF-MP		Target wt% of each oxide in CAF-MP
Al ₂ O ₃	1.27	MoO ₃	0.85
BaO	12.76	Nd ₂ O ₃	5.23
CaO	1.39	Pr ₂ O ₃	1.45
Cr ₂ O ₃	6.33	SeO ₂	0.08
CdO	0.11	Sm ₂ O ₃	1.08
Ce ₂ O ₃	3.10	SnO ₂	0.07
Cs ₂ O	2.88	SrO	0.98
Eu ₂ O ₃	0.17	TeO ₂	0.66
Fe ₂ O ₃	6.65	TiO ₂	49.16
Gd ₂ O ₃	0.16	Y ₂ O ₃	0.63
La ₂ O ₃	1.58	ZrO ₂	2.99

Table 2.

T_m	T	t_{eq} (h)		
1500°C	1500°C	4		
1500°C	1325°C	1	12	24
1500°C	1285°C	1	12	24

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

(a)

(b)

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14