

# Radiation damage of hollandite in multiphase ceramic waste forms



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## ABSTRACT

Radiation damage was simulated in multiphase titanate-based ceramic waste forms using an ion accelerator to generate high energy alpha particles ( $\text{He}^+$ ) and an ion implanter to generate 7 MeV gold ( $\text{Au}^{3+}$ ) particles. X-ray diffraction and transmission electron microscopy were used to characterize the damaged surfaces and nearby regions. Simulated multiphase ceramic waste forms were prepared using two processing methods: spark plasma sintering and melt-processing. Both processing methods produced ceramics with similar phase assemblages consisting of hollandite-, zirconolite/pyrochlore-, and perovskite-type phases. The measured heavy ion ( $\text{Au}^{3+}$ ) penetration depth was less in spark plasma sintered samples than in melt-processed samples. Structural breakdown of the hollandite phase occurred under  $\text{He}^+$  irradiation indicated by the presence of x-ray diffraction peaks belonging to  $\text{TiO}_2$ ,  $\text{BaTiO}_5$ , and other hollandite related phases ( $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ). The composition of the constituent hollandite phase affected the extent of damage induced by  $\text{Au}^{3+}$  ions.

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## 1. Introduction

Ceramic waste forms are candidates for the immobilization of high-level waste (HLW) generated by reprocessing of commercial used nuclear fuel (UNF). Ceramics have been investigated for their potential advantages over glass waste forms such as higher waste loading of elements that have low solubility in glasses and improved chemical durability [1,2]. Titanate-based ceramic materials, specifically those in the SYNROC family, have been studied for the HLW containment [3–5] as these multiphase assemblages can accommodate elements with a wide range of valences and ionic sizes in the crystal lattices [5] within the waste form.

SYNROC materials are traditionally prepared via hot isostatic pressing (HIP), but alternative fabrication methods such melt-processing and spark plasma sintering (SPS) offer potential advantages over HIP. Melt-processing of ceramics would be simplified compared to HIP methods and melter technologies have been successfully demonstrated for several decades as the preferred option to vitrify of HLW throughout the world. A distinct advantage

of SPS compared to HIPing is the potential to reduce volatilization owing to short processing times (can be < 30 min) that can be achieved.

Ceramics have been shown to be susceptible to damage induced by  $\alpha$ -radiation [6–8]. Specifically,  $\alpha$ -radiation can induce atomic displacements that lead to structural rearrangements affecting the physical and chemical properties of the material. An  $\alpha$ -decay event consists of the release of an  $\alpha$ -particle (light particle) and a recoil nucleus (heavy particle). Actinides and their daughter products have long half-lives and therefore  $\alpha$ -decay becomes dominant over long time scales. This necessitates the need to use ion implantation techniques to study the effects of  $\alpha$ -decay on a laboratory time scale. One method to study these differing damage mechanisms is by using  $\text{He}^+$  ions to simulate  $\alpha$ -particles and heavy ions, such as  $\text{Au}^{3+}$  or  $\text{Kr}^{3+}$ , to simulate  $\alpha$ -recoils.

Charged particle implantation has been widely utilized to study radiation damage in crystalline ceramics [9–13]. However, relatively few studies have been performed on multiphase crystalline ceramics for nuclear waste immobilization of a combined waste to include a Cs/Sr separated waste stream, the Trivalent Actinide - Lanthanide Separation by Phosphorous reagent Extraction from Aqueous Komplexes (TALSPEAK) waste stream, the transition metal

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fission product waste stream resulting from the transuranic extraction (TRUEX) process, MoO<sub>3</sub>, and noble metals [14–17]. Although the materials modeled were inert matrix fuel and not waste forms, Men et al. studied the radiation response of a four-phase oxide ceramic composite using Au and Xe ions [18]. The Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub>, and MgAl<sub>2</sub>O<sub>4</sub> phases exhibited high amorphization resistance when irradiated with 10<sup>20</sup> ions/m<sup>2</sup> 10 MeV Au ions and 10<sup>16</sup>–10<sup>17</sup> ions/m<sup>2</sup> Xe ions.

In the present paper, we report results on the effects of radiation damage in multiphase titanate-based simulated waste forms containing hollandite, perovskite, and pyrochlore/zirconolite/zirconium-rich phases produced by SPS and melt-processing. Single phase hollandite material produced by solid state sintering is also presented for comparison. The radiation resistance was compared via irradiation with light (He<sup>+</sup>) and heavy (Au<sup>3+</sup> or Kr<sup>3+</sup>) ions and characterized using grazing incidence x-ray diffraction (GIXRD) and transmission electron microscopy (TEM).

## 2. Experimental

The ceramic waste form compositions were developed by Savannah River National Laboratory (SRNL) and are listed in Table 1. The compositions targeted hollandite phase with metal oxide additions of Cr, Al, and Fe (designated CAF-MP) and hollandite phase with only Cr additions (designated Cr-MP). Samples were prepared by melt-processing and SPS methods that have been documented previously [19]. The compositions prepared by SPS were heated to a maximum temperature of 1125 °C (Cr-MP) or 1000 °C (CAF-MP), as read by an optical pyrometer focused on the outside of the die and held at temperature for 3 min. Melt-processed samples were ramped to 1500 °C and held for 30 min (both compositions). Single phase Cr-hollandite (Ba<sub>1.15</sub>Cr<sub>2.3</sub>Ti<sub>5.7</sub>O<sub>16</sub>, designated Cr-HOL) was produced via solid state sintering stoichiometric amounts of commercially available oxides/carbonates that were mixed, ball-milled and dried at ~ 120 °C to form the precursor batch. The resulting powders were compacted into pellets and subsequently sintered at 1100 °C for 4 h. Solid-state synthesis (SSS) was performed, as opposed to SPS, because composition was found to have a greater impact on amorphization behavior than processing.

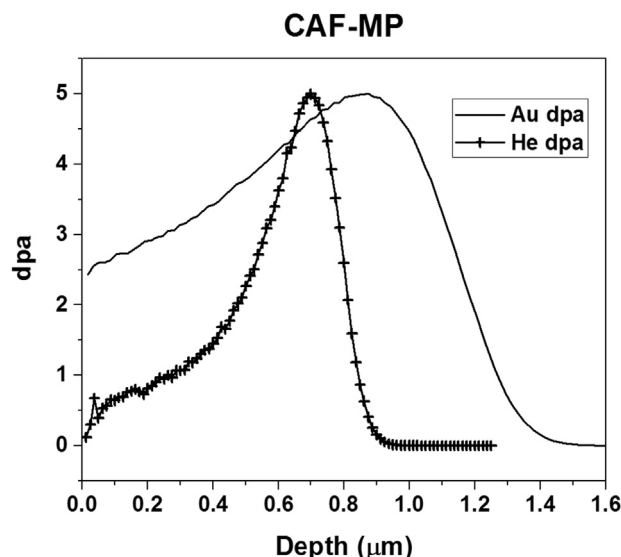
**Table 1**  
Simulated waste form compositions.

Oxide	CAF-MP (wt%)	Cr-MP (wt%)	Cr-HOL (wt%)
Al <sub>2</sub> O <sub>3</sub>	1.27	0.00	0.00
BaO	12.76	12.72	28.70
CaO	1.39	1.38	0.00
Cr <sub>2</sub> O <sub>3</sub>	6.33	14.5	21.73
CdO	0.11	0.11	0.00
Ce <sub>2</sub> O <sub>3</sub>	3.10	3.09	0.00
Cs <sub>2</sub> O	2.88	2.87	0.00
Eu <sub>2</sub> O <sub>3</sub>	0.17	0.17	0.00
Fe <sub>2</sub> O <sub>3</sub>	6.65	0.00	0.00
Gd <sub>2</sub> O <sub>3</sub>	0.16	0.16	0.00
La <sub>2</sub> O <sub>3</sub>	1.58	1.58	0.00
MoO <sub>3</sub>	0.85	0.84	0.00
Nd <sub>2</sub> O <sub>3</sub>	5.23	5.22	0.00
Pr <sub>2</sub> O <sub>3</sub>	1.45	1.44	0.00
Rb <sub>2</sub> O	0.42	0.42	0.00
SeO <sub>2</sub>	0.08	0.08	0.00
Sm <sub>2</sub> O <sub>3</sub>	1.08	1.07	0.00
SnO <sub>2</sub>	0.07	0.07	0.00
SrO	0.98	0.98	0.00
TeO <sub>2</sub>	0.66	0.65	0.00
TiO <sub>2</sub>	49.16	49.01	49.57
Y <sub>2</sub> O <sub>3</sub>	0.63	0.63	0.00
ZrO <sub>2</sub>	2.99	2.98	0.00

Samples for ion irradiation experiments were prepared by polishing a surface to 1 μm using a diamond suspension. The radiation dose in these materials was estimated using the Stopping and Range of Ions in Matter (SRIM) program [20]. The displacements per atom (dpa) as a function of depth for CAF-MP (similar results are obtained for Cr-MP) using 7 MeV Au<sup>3+</sup> and 200 keV He<sup>+</sup> is shown in Fig. 1. The peak in dpa (5, 0.5 or 0.05) is located at 870 nm (Au<sup>3+</sup>) and 700 nm (He<sup>+</sup>). The dpa is adjusted by changing the fluence of the incoming gold ions (ions/m<sup>2</sup>).

The experiments using Au<sup>3+</sup> ions were carried out at room temperature at the Environmental Molecular Sciences Laboratory (EMSL), Pacific Northwest National Laboratory (PNNL) and the experiments using He<sup>+</sup> ions at the Ion Beam Materials Lab (IBML), Los Alamos National Laboratory (LANL) for the multiphase materials. 7 MeV Au<sup>3+</sup> implantations were performed at EMSL on a National Electrostatics Corporation (NEC) model 9SDH-2 3.4 MV tandem accelerator [21] simulating three damage levels in SPS samples: 0.05, 0.5 and 5 dpa and one damage level, 5 dpa, in melt-processed samples. These values were chosen to simulate varying storage times, from approximately 10<sup>2</sup>–10<sup>6</sup> years [22]. The implanted area was 6 × 6 mm for both melt-processed and SPS samples. 200 keV He<sup>+</sup> implantations were performed at IBML using a 200 kV Danfysik high current ion implanter at a dose of 5 dpa to simulate α-particle damage after long storage times. 380 keV He<sup>+</sup> and 3 MeV Kr<sup>3+</sup> implantations were performed on single phase hollandite using the Ion Beam Laboratory at the University at Albany. Single phase hollandites received doses of 0.5 dpa of either He<sup>+</sup> or Kr<sup>3+</sup> ions. The details of implantation experiments are summarized in Table 2.

Powder x-ray diffraction (XRD) was carried out using a D-2 Phaser (Bruker, Massachusetts, USA) for phase identification. GIXRD was performed on implanted samples using a grazing angle of 2° on the EMSL (Au<sup>3+</sup>) samples and 1° for the LANL (He<sup>+</sup>) samples with a Bruker AXS D8 Advance (Bruker, Massachusetts, USA) instrument using Cu Kα radiation in theta – 2 theta geometry. A plot of x-ray penetration depth vs grazing angle is shown in Fig. 2. The unirradiated areas of the Au<sup>3+</sup> samples were visible and ground off prior to measurement. Damaged cross-section specimens were prepared for transmission electron microscopy (TEM) by using the lift-out method with a focused ion beam (FIB). The damaged areas were examined using a FEI Tecnai F20 TEM operating at 200 kV.



**Fig. 1.** Damage profile in CAF-MP using 7 MeV Au<sup>3+</sup> and 200 keV He<sup>+</sup> ions.

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