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Characterisation of zirconolites prepared under different processing atmospheres

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1 Introduction

The inventory of UK-owned plutonium (Pu) is forecast to peak at 140 teHM. A fraction of the Pu inventory has been declared unsuitable for MOX fabrication, due to chlorine contamination arising from long term storage in polyvinyl chloride (PVC) packaging containment [1]. An alternative approach is the conditioning of the Pu stockpile and waste material via immobilisation within a ceramic matrix.

Zirconolite (prototypically $CaZrTi_2O_7$) is being considered as a potential ceramic wasteform for the immobilisation of plutonium due to its aqueous durability and chemical flexibility [2]. The understanding of the oxidation state of Pu within zirconolite is essential to predict the long-term stability and feasibility of zirconolite. In this work, two atmospheres were employed to prepare zirconolite wasteforms with composition $Ca_{0.8}Ce_{0.2}ZrTi_{1.6}Cr_{0.4}O_7$, using Ce as the surrogate of Pu and Cr for charge compensation. The oxidation state of Ce in the samples was examined and compared.

2 Experiment

Reagent grade oxides ($CaTiO_3$, ZrO_2, Cr_2O_3, TiO_2 and CeO_2) were batched and mixed, according to the target composition ($Ca_{0.8}Ce_{0.2}ZrTi_{1.6}Cr_{0.4}O_7$). The oxide precursors were reaction sintered under two atmospheres: (1) at 1350ºC for 20 h in air; and (2) at 1320ºC for 30 min in a reducing environment using spark plasma sintering (SPS) [3]. Specimens were prepared for XANES measurement by homogenising and suspending in polyethylene glycol to produce samples with a thickness of *ca.* one absorption length. Ce L_{III} edge XANES spectra were acquired in transmission mode on BL-27 at the Photon Factory (Tsukuba, Japan). Spectra were also acquired on CeO_2 and $CePO_4$ standards. Subsequent data reduction and analysis, was performed using the Athena software package [4].

3 Results and Discussion

A zirconolite-2M phase (space group C2/*c*) was detected as the major product after sintering $Ca_{0.8}Ce_{0.2}ZrTi_{1.6}Cr_{0.4}O_7$ in air. The presence of $CaTiO_3$ (1.2 ± 0.2 wt%) and Cr_2O_3 (0.6 ± 0.2 wt%) were determined by Rietveld refinement. In the SPSed sample, 19.3 ± 0.4 wt% $CaTiO_3$ was detected alongside the major zirconolite-2M phase.

Fig. 1 shows the Ce L_{III} edge XANES data for the zirconolite samples overlaid with the standards. It was apparent from visual inspection that Ce was present mainly as Ce^{4+} in the air-sintered sample, which is a good analogue for Pu^{4+}. Closer inspection of the data revealed a small shift in the edge position toward lower energy (with respect to CeO_2) and a small change in the relative intensity of the asymmetric doublet feature on the crest of the absorption edge, consistent with the presence of a minor fraction of Ce^{3+}. Linear combination fitting using the CeO_2 and $CePO_4$ standards, indicated the presence of $16.4 \pm 1.1\%$ Ce^{3+} and 83.6 ± 1.5 % Ce^{4+}. The spectrum for the SPS sample consisted of a single intense feature consistent with the Ce^{3+} standard. Linear combination analysis determined that a complete reduction to the Ce^{3+} species had been achieved. These results indicates that the selection of the processing atmosphere has a significant impact on phase assemblage and Ce oxidation state. Further investigation on the minimisation of the secondary phase, which is undesirable, and the aqueous durability of zirconolite is underway.

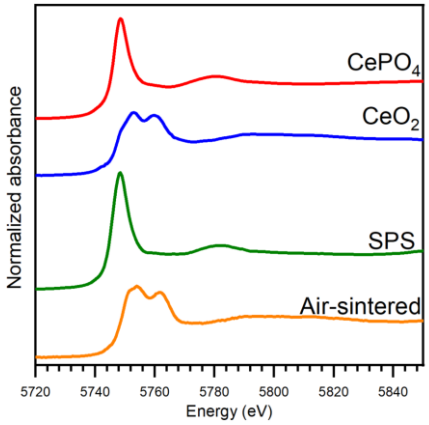

Fig. 1: Ce L_{III} edge XANES data for $Ca_{0.8}Ce_{0.2}ZrTi_{1.6}Cr_{0.4}O_7$ samples processing under different atmosphere. Ce standards of known oxidation state are also shown for comparison.

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