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## Synthesis and characterization of brannerite wastefoms for the immobilization of mixed oxide fuel residues

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### Abstract

A possible method for the reduction of civil Pu stockpiles is the reuse of Pu in mixed oxide fuel (MOX). During MOX fuel production, residues unsuitable for further recycle will be produced. Due to their high actinide content MOX residues require immobilization within a robust host matrix. Although it is possible to immobilize actinides in vitreous wastefoms; ceramic phases, such as brannerite ( $UTi_2O_6$ ), are attractive due to their high waste loading capacity and relative insolubility. A range of uranium brannerites, formulated  $Gd_xU_{1-x}Ti_2O_6$ , were prepared using a mixed oxide route. Charge compensation of divalent and trivalent cations was expected to occur via the oxidation of  $U^{4+}$  to higher valence states ( $U^{5+}$  or  $U^{6+}$ ).  $Gd^{3+}$  was added to act as a neutron absorber in the final Pu bearing wastefom. X-ray powder diffraction of synthesised specimens found that phase distribution was strongly affected by processing atmosphere (air or Ar). In all cases prototypical brannerite was formed accompanied by different secondary phases dependent on processing atmosphere. Microstructural analysis (SEM) of the sintered samples confirmed the results of the X-ray powder diffraction. The preliminary results presented here indicate that brannerite is a promising host matrix for mixed oxide fuel residues.

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## 1. Introduction

Several countries have large stockpiles of plutonium. A possible method for the reduction of Pu stockpiles is the use of mixed oxide fuel (MOX) to produce power in civilian, thermal nuclear reactors. Mixed oxide fuels are composed of a mixture of uranium and plutonium oxides, typically 90-95 % U and 5 - 10% Pu<sup>(1)</sup>. Although highly recyclable, some residues arising from the production of MOX fuels will eventually require disposal. Ceramic phases are particularly attractive for actinide bearing wastes due to their ability to incorporate a high actinide waste loadings. Brannerite,  $UTi_2O_6$ , is a monoclinic phase with space group  $C2/m$  commonly found as an accessory mineral in uranium deposits and multiphase ceramic wasteforms designed for disposal of actinide bearing wastes<sup>(2,3)</sup>. The brannerite structure consists of layers of  $TiO_6$  octahedra with larger cations located between the layers, natural brannerites exhibit considerable chemical flexibility with elements such as Ca, Y, Pb, Ce and Th being incorporated on the U site and Fe, Si and Al substituting on the Ti site. Although natural samples are often found to be completely metamict, the presence of brannerite in vial sediments after the weathering of host rocks indicates that brannerites possess sufficient aqueous durability for consideration as potential host matrices for actinide bearing wastes<sup>(4,5)</sup>.

In this study, the production of brannerites suitable for MOX disposal was investigated by synthesising brannerites with a range of Gd contents ( $Gd_xU_{1-x}Ti_2O_6$ ) under different atmospheres in an attempt to find a suitable baseline composition and processing conditions. Previous studies have shown that although synthesis of stoichiometric brannerite requires inert conditions it is possible to stabilize the brannerite structure in air by the addition of dopants (Ca, La, Gd)<sup>(6-8)</sup>.

## 2. Materials and methods

### 2.1. Materials synthesis

Brannerites with composition  $Gd_xU_{1-x}Ti_2O_6$  were synthesised via the oxide route under oxidizing or inert atmospheres (air or argon). Waste loadings were varied across the compositions with varying levels of Gd added to act as a neutron absorber for the final Pu bearing wasteform ( $x = 0.1, 0.2$  and  $0.3$ ). Charge balancing of trivalent cations was expected to occur via the oxidation of U(IV) to higher oxidation states (U(V), U(VI)) as observed in previous investigations<sup>(7,8)</sup>.

Stoichiometric amounts of oxide precursors ( $UO_2$ ,  $Gd_2O_3$ ,  $TiO_2$ ) were mixed with isopropanol to form a slurry and ball milled using a Fritsch Pulverisette 23 for five minutes at a frequency of 30 Hz. The milled slurry was then dried in an oven. Sintered pellets were produced by uniaxially pressing 0.6 g of material in a hardened steel die with a load of 2 tons to form a green body followed by reaction under flowing air or argon at 1320 °C for 24 hours.

### 2.2. Materials characterization

Sintered brannerites were ground and characterized by x-ray powder diffraction using a Bruker D2 Phaser in Bragg-Brentano geometry with a Cu source and Ni foil  $K\beta$  filter. Lattice parameters were found by performing a Le Bail refinement of the data.

Microstructure and phase distribution of sintered pellets was investigated by scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM-EDX) using a Hitachi TM3030 SEM equipped with a Bruker Quantax EDX detector. Samples were prepared for SEM analysis by mounting in cold setting resin and polishing with progressively finer SiC paper and diamond pastes to an optical finish (1  $\mu m$ ). Samples were sputter coated with carbon to reduce surface charging effects.

### 3. Results and discussion

#### 3.1. Air sintered samples

All synthesised brannerites were characterized by powder x-ray diffraction and scanning electron microscopy. X-ray diffraction found sharp peaks indicative of prototypical brannerite for all compositions. The secondary phases  $U_3O_8$  and rutile ( $TiO_2$ ) were also observed and found to vary with the level of Gd substitution, see Figure 1. As Gd substitution was increased the relative intensities of  $U_3O_8$  and rutile decreased whereas the intensity of the brannerite peaks was found to increase indicating a higher yield of brannerite. The brannerite microstructure observed by scanning electron microscopy closely matched that indicated by x-ray diffraction. As can be seen in Figure 2, the relative proportions of brannerite,  $U_3O_8$  and rutile vary with the level of Gd substitution. As Gd substitution increases, the amount of brannerite formed increases and the amount of  $U_3O_8$  and rutile present decreases, in agreement with XRD data.

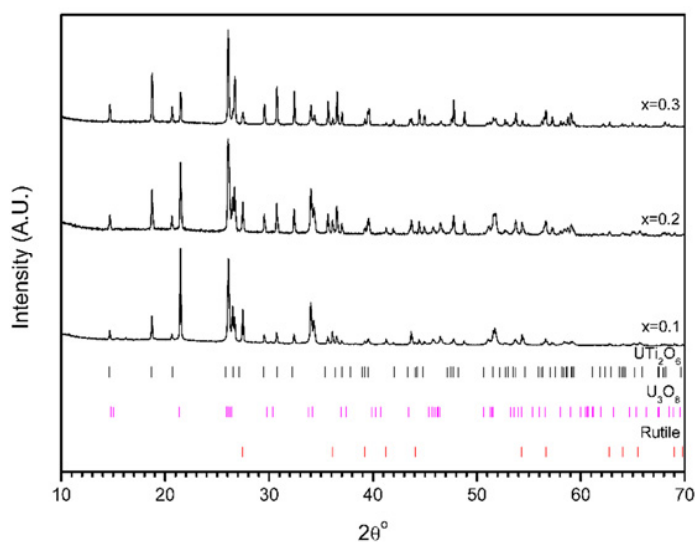


Figure 1: X-ray powder diffraction data for  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in air at 1320 °C

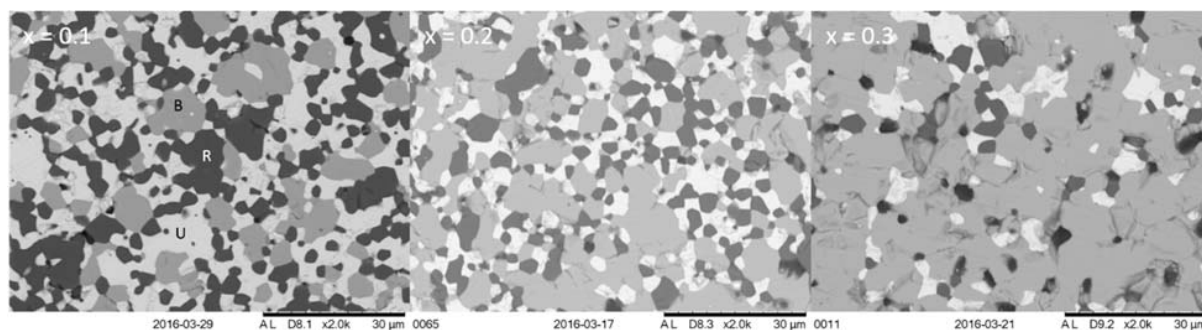


Figure 2: Representative backscattered electron images for  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in air at 1320 °C.  
B = Brannerite, R = Rutile, U =  $U_3O_8$ .

Sintering samples in air was found to result in the formation of three distinct phases; brannerite,  $U_3O_8$  and rutile ( $TiO_2$ ). Patchett and Nuffield (1960) found that sintering stoichiometric brannerite batches in air results in the formation of rutile and  $U_3O_8$  (6); it would therefore appear that the addition of Gd stabilizes the formation of the brannerite phase in air. These results are in agreement with both Vance et al (2001) and James and Watson (2002) who also found that Gd stabilized the formation of brannerite in air and that Gd-substituted brannerites with  $x \leq 0.3$  formed a mixture of brannerite,  $U_3O_8$  and rutile (7,8).

SEM-EDX was used to study the elemental distribution of brannerites synthesised in air, typical results are shown in Figure 3. Uranium was found to be localised in the  $U_3O_8$  and brannerite phases with no incorporation apparent within regions identified as rutile. Similar to U, Ti was found to be localized in the rutile and brannerite phases with no incorporation apparent within regions identified as  $U_3O_8$ . Gd was found to be present throughout the samples but is preferentially incorporated into the brannerite phase and not the  $U_3O_8$  or rutile phases.

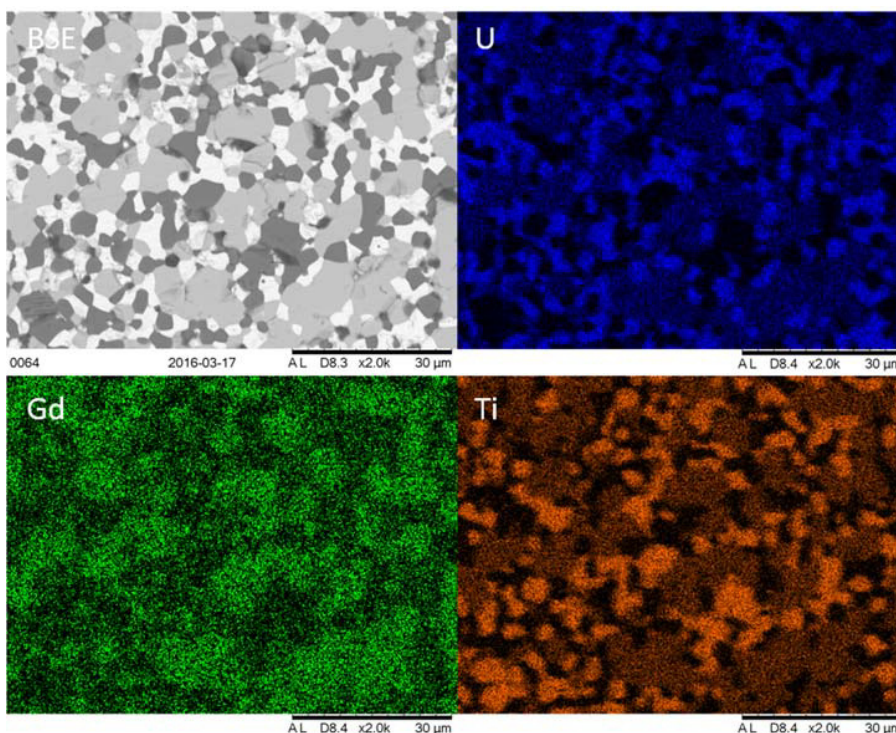


Figure 3: Representative backscattered electron image and EDX maps of U, Gd and Ti for  $Gd_{0.2}U_{0.8}Ti_2O_6$  sintered in air at 1320 °C.

### 3.2. Air sintered samples

Sintering samples under an argon atmosphere resulted in a different phase assemblage to that observed for air fired samples. When analysed by XRD, sharp peaks indicative of prototypical brannerite were found in all cases however, it was found that the level of Gd substitution affected the final phase assemblage. As shown in figure 4, samples with  $x = 0.1$  were found to form near single phase brannerite, inclusions of unreacted  $UO_2$  and rutile were also observed. Samples with  $x = 0.2$  or  $0.3$  did not show evidence of retained  $UO_2$  but were instead found to contain an additional pyrochlore phase (major peaks evident at approximately 15, 31 and 39 °2 $\theta$ ) and minor inclusions of rutile. Considering the relative intensities of the pyrochlore peaks observed, it would appear that increasing Gd substitution simply results in the formation of a greater amount of the pyrochlore phase. Multiple heat treatments at 1320 °C and duplicated experiments at 1400 °C, see Figure 5, did not result in more favourable phase assemblages indicating that the observed phase assemblages are most likely not a result of kinetic factors and more likely the result of compositional effects. These results are supported by the microstructures observed by electron microscopy.

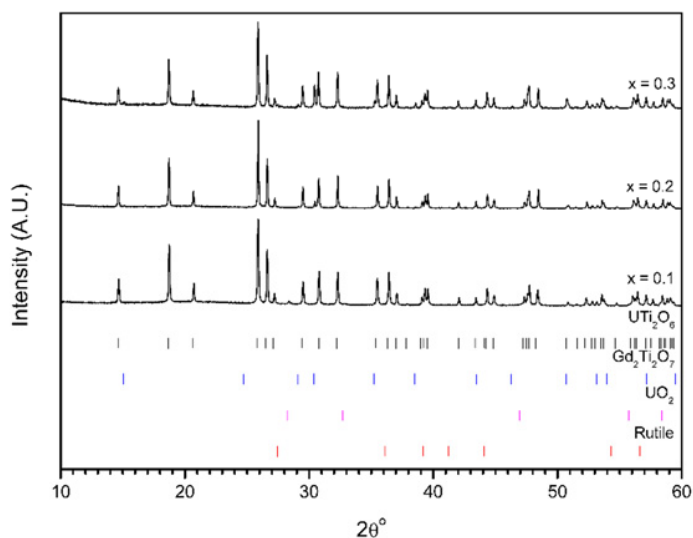


Figure 4: X-ray powder diffraction data for  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in argon at 1320 °C

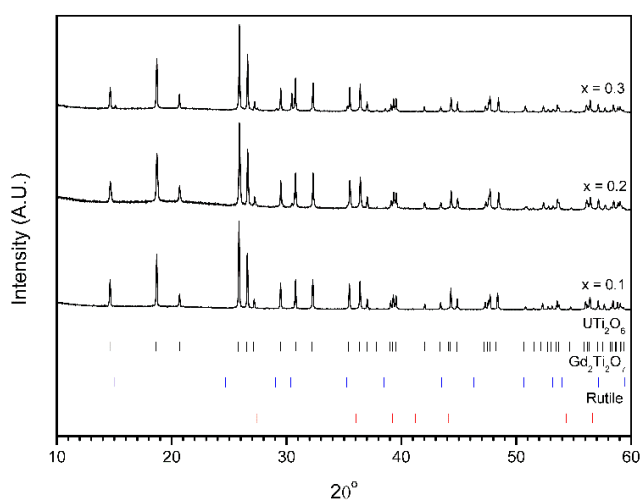
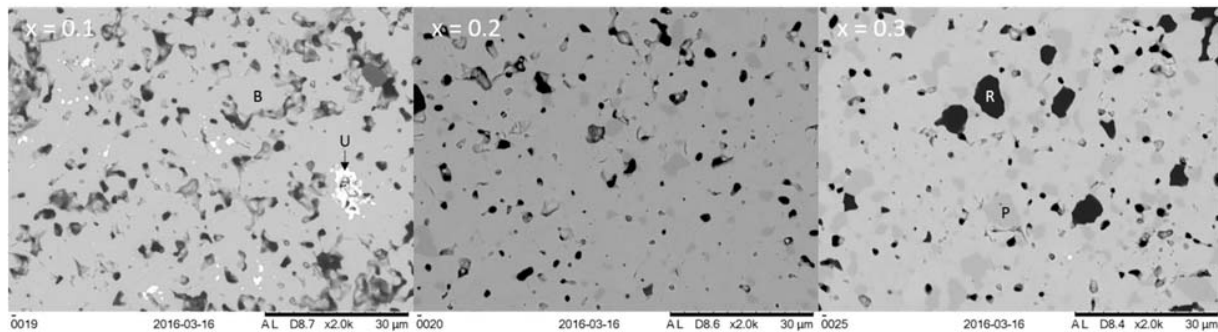
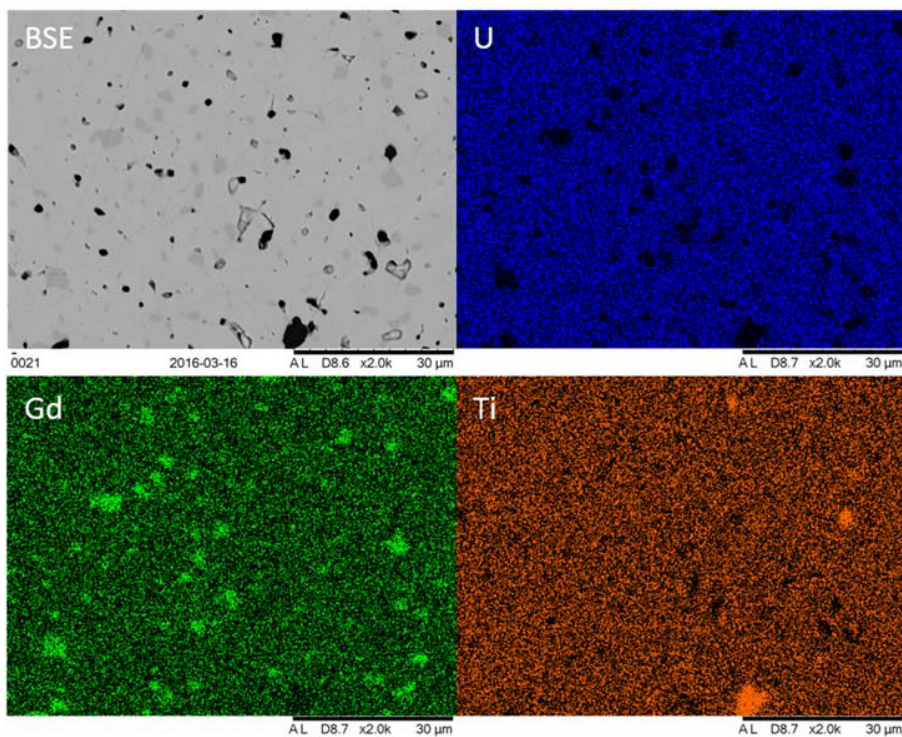


Figure 5: X-ray powder diffraction data for  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in argon at 1400 °C

The refined lattice parameters, see Table 1, suggest that despite increasing amounts of Gd being added to the initial batch; no extra Gd is incorporated into the brannerite structure with increasing Gd substitution. Considering the respective ionic radii of U(IV) and Gd (III) in six-fold co-ordination (0.89 and 0.938 Å<sup>(9)</sup>); it would be expected that the incorporation of increasing amounts of Gd would result in an increase in the lattice parameters of the unit cell, as can be seen there is no notable variation in the lattice parameters with respect to Gd substitution.

Table 1: Refined lattice parameters for the  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in inert atmospheres

x	a	b	c	$\beta$
0.1	9.8199(2)	3.7648(1)	6.9232(1)	118.841(1)
0.2	9.8190(2)	3.7591(1)	6.9170(1)	118.794(1)
0.3	9.8203(2)	3.7592(1)	6.9176(1)	118.787(1)

Figure 6: Representative backscattered electron images for  $Gd_xU_{1-x}Ti_2O_6$  compositions sintered in air at 1320 °C. B = Brannerite, P = Pyrochlore, R = Rutile, U =  $UO_2$ .Figure 7: Representative backscattered electron image and EDX maps of U, Gd and Ti for  $Gd_{0.2}U_{0.8}Ti_2O_6$  sintered in argon at 1320 °C.

As can be seen in Figure 6, increasing Gd substitution leads to the formation of greater amounts of a secondary phase, this was determined to be the pyrochlore phase found by x-ray diffraction.

Figure 7 shows the typical elemental distribution of Gd-substituted brannerites with  $x \geq 0.2$  synthesised under inert atmospheres. As can be seen, although brannerite is present as a majority phase, the secondary pyrochlore phase is present throughout the sample. Gd is present throughout the sample however, the concentration of Gd within the pyrochlore phase may result in decreased criticality performance for a final wasteform.

The results reported in this study are in contrast to those reported by both Vance et al (2001) and James and Watson (2002)<sup>(7,8)</sup>. The solid solution limit of Gd in brannerite synthesized in Ar quoted by James and Watson,  $0 < x < 0.45$ , does not correlate with the observations from this work which indicate that the solubility limit of Gd is  $< 0.2$  formula units. These findings are clearly evidenced by the X-ray diffraction and scanning electron microscopy data.

#### 4. Conclusions

This study has found that the synthesis of brannerite compositions for MOX residue disposal requires careful control of the system stoichiometry and processing conditions. Sintering material in air produces an unfavourable mixture of brannerite,  $U_3O_8$  and rutile. Increasing substitution of Gd for U improves the final observed phase assemblage. However, in order to achieve a single phase wasteform, the level of substitution would have to be such that the final waste loading of any wasteform would be significantly reduced. When brannerites are synthesised in inert atmospheres, the level of Gd substitution has been shown to have a strong effect on the final phase assemblage. Substitution of  $\geq 0.2$  formula units of Gd results in the formation of a parasitic pyrochlore phase that preferentially incorporates Gd.

Although this study has investigated the synthesis of Gd substituted uranium brannerites, the behaviour of plutonium in a final wasteform remains uncertain. Further investigation using either a surrogate, e.g. Ce, or plutonium is necessary to be certain of the solid state chemistry of a final MOX wasteform.

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