

Synthesis and characterisation of high ceramic fraction brannerite (UTi₂O₆) glass-ceramic composites

M C Dixon Wilkins¹, E R Maddrell², M C Stennett¹ and N C Hyatt^{1*}

¹ Department of Materials Science & Engineering, The University of Sheffield, Mappin Street, Sheffield, S1 3JD.

² National Nuclear Laboratory, Sellafield, Cumbria, UK

*n.c.hyatt@sheffield.ac.uk

Abstract. Brannerite, UTi₂O₆, glass-ceramic composites have been prepared, using UO₂ and TiO₂ as the ceramic phase precursors. A range of cold-press and sinter samples with varying glass:ceramic ratios have been prepared under argon at 1200 °C to investigate the effect of glass content on formation of brannerite. Ceramic brannerite formed well in all compositions, even at low (10% by weight) glass fractions, with UO₂ as a minor product. Three further brannerite glass-ceramics have been prepared by hot isostatic pressing to investigate the compatibility of this system to HIPing. The samples HIPed at 1200 °C form brannerite, with UO₂ as a minor phase with slightly higher abundance than in the cold-press and sinter samples.

1. Introduction

Brannerite (prototypically UTi₂O₆) is a naturally occurring mineral, notable for having a particularly high uranium content (> 55% by weight uranium) and being highly durable. Natural samples of brannerite have been found to retain the majority of their uranium inventory, even when they have been completely amorphised (*i.e.* they are metamict) and altered over time [1]. These properties make brannerite a possible candidate material for immobilisation of high actinide content nuclear wastes, as they are evidence that a brannerite host matrix may have a high waste loading and aqueous durability.

The properties of ceramic wasteforms (such as brannerite) make them excellent hosts for certain waste streams; however, their more limited chemical flexibility (especially compared to vitreous or encapsulating technologies) reduces the possible applications to those waste streams that are already reasonably pure. This lack of chemical flexibility can be remedied by the addition of a secondary vitreous phase, resulting in a glass-ceramic (where the ceramic phase crystallises from the glass during an annealing step) or glass-ceramic composite (where the glass and ceramic phases may either form at the same time, or both be pre-formed, and simply sintered together) depending on the processing route.

Glass-ceramic wasteform materials have many benefits when compared to single-phase ceramic wasteforms. Primarily is the wider range of wastes that the system may feasibly immobilise, where the inclusion of a glass phase with low actinide solubility does not preclude a suitable wasteform, as the actinide will partition into the ceramic phase. An often overlooked factor is the reduction in processing temperature caused by addition of the glass phase during synthesis. For example, uranium brannerite ceramics require temperatures of 1350 °C or higher for an extended duration to form [2–5], but various



brannerite-structured ceramic phases within a glass-ceramic composite system have been shown to form at 1200 °C [6–9].

This is especially important when considering the compatibility of these materials with thermal processing techniques. In this study hot isostatic pressing (HIP or HIPing) has been used to consolidate these materials. The temperature of formation is of particular importance for HIP, as the most common and easily available canister material is stainless steel, with a maximum HIPing temperature of 1300 °C; so it is desirable to reduce the reaction temperature *e.g.* through the addition of a glass phase.

In this study UTi_2O_6 glass-ceramics have been produced by two separate methods to investigate the viability of HIP as a processing route. Starting from the component oxides (UO_2 , TiO_2) and a glass precursor, a cold-press and sinter (CPS) method has been used to examine how this lowered temperature of formation may be dependent on the relative abundance of the vitreous phase, and preliminary HIP samples have been prepared as an initial proof-of-concept.

2. Experimental

2.1. Production of glass-ceramics

All samples were prepared using UO_2 and TiO_2 to form the ceramic phase, and a pre-calcined glass precursor to form the vitreous phase. The glass precursor was formed by calcining a homogeneous mixture (targeting a glass composition of $Na_2AlBSi_6O_{16}$) of the glass reagents (Na_2CO_3 , H_3BO_3 , Al_2O_3 , and SiO_2) at 600 °C for 6 hours to remove volatile species. The ceramic components and the glass precursor were then wet milled together in isopropanol to homogenise. The resulting slurry was dried at 90 °C, and the powders retrieved for further processing.

Samples prepared by a CPS route were prepared by pressing into pellets (approximately 250 mg each) and then heat treated on a bed of coarse ZrO_2 (to prevent them from sticking to the crucibles) at 1200 °C for 12 hours, under an Ar atmosphere.

Samples prepared by HIP were prepared by first calcining the as-milled powders at 600 °C to remove any remaining volatiles. The powders were then pressed into stainless steel HIP canisters under approximately 1 ton using a hydraulic press (each canister contained approximately 25 g of material). The can lids were welded on, and the cans evacuated under vacuum at 600 °C to further ensure removal of all volatile materials. The evacuation tube was then crimped off and welded shut. The prepared cans were then HIPed at 100 MPa at the desired temperature and time.

Table 1 contains the as-batched compositions of all samples, as well as the U:Ti molar ratio and details of all heat treatments.

2.2. Characterisation

All samples were characterised using powder X-ray diffraction (XRD, Bruker D2 Phaser, Ni-filtered $Cu K\alpha$), and scanning electron microscopy (SEM, Hitachi TM3030 with Bruker Quantax EDX system). Samples were prepared for SEM by mounting and polishing to an optical finish using successive grades of abrasive paper and diamond suspensions.

Table 1. As-batched compositions (% by weight) of brannerite glass-ceramics, along with details of their heat treatment.

Sample ID	Glass	UO ₂	TiO ₂	U:Ti molar ratio	Heat treatment
CPS50	50%	31.42%	18.58%	1:2	1200 °C, 12 h, Ar
CPS60	40%	37.70%	22.30%	1:2	
CPS70	30%	43.98%	26.02%	1:2	
CPS80	20%	50.27%	29.73%	1:2	
CPS90	10%	56.55%	33.45%	1:2	
HIP1100	50%	31.42%	18.58%	1:2	HIP, 1100 °C, 24 h
HIP1200a	50%	31.42%	18.58%	1:2	HIP, 1200 °C, 4 h
HIP1200b	48.75%	30.63%	20.62%	1:2.277	

3. Results and discussion

3.1. The effect of glass-ceramic ratio on the formation of brannerite

The compositions that were processed by a CPS route show broadly the same phase assemblage. The XRD patterns all confirm that brannerite, UTi₂O₆, was formed as the predominant crystalline product, along with a small amount of unreacted UO₂ (less than 2% by weight). As the ratio of glass to ceramic is changed from 50:50 (by weight) to 10:90 the relative amount of UO₂ increases, but still remains a minor phase (see Figure 2).

The microstructures seen in the SEM micrographs are in good agreement with the XRD phase assemblages. As the glass content decreases from sample CPS50 to sample CPS90, the observed microstructures show increasing amounts of brannerite, with a corresponding increase in the amount of UO₂ also observed. In all samples, the majority of UO₂ is seen as small regions encapsulated within grains of brannerite, with a smaller amount of UO₂ particles held directly within the glass phase. Macroscale pores are visible in all samples; these are most likely due to incomplete calcination of the glass precursor causing some volatiles to only be removed during the final heat treatment at 1200 °C, rather than during the glass precursor forming pre-calcination at 600 °C (see Figure 1).

The presence of excess unreacted UO₂ is unsurprising; previous reports of brannerite glass-ceramics in the literature have noted that addition of superstoichiometric amounts of the titanium starting material is necessary to prevent formation of these regions of UO₂. This may be due to one or more different factors, depending on choice of processing route. Dissolution of TiO₂ in the glass phase during heat treatment may prevent full reaction of the uranium, loss of titanium during processing will also have the same effect (especially relevant for alkoxide/nitrate based routes, where titanium isopropoxide will readily hydrolyse in air during sample preparation), or some level of A-site non-stoichiometry in the final brannerite phase (which has previously been observed in natural and synthetic brannerites alike [1,10]).

As the relative glass content decreases from 50% to 10% by weight, the temperature dependence of brannerite formation appears to be unaffected. This is evidenced by the majority crystalline product in all samples being brannerite, with no remaining crystalline TiO₂ observed in the diffraction patterns or SEM micrographs. This shows that this glass-ceramic composite system forms well at processing temperatures achievable in standard stainless steel HIP canisters, and so three preliminary HIPed samples have also been prepared to confirm this.

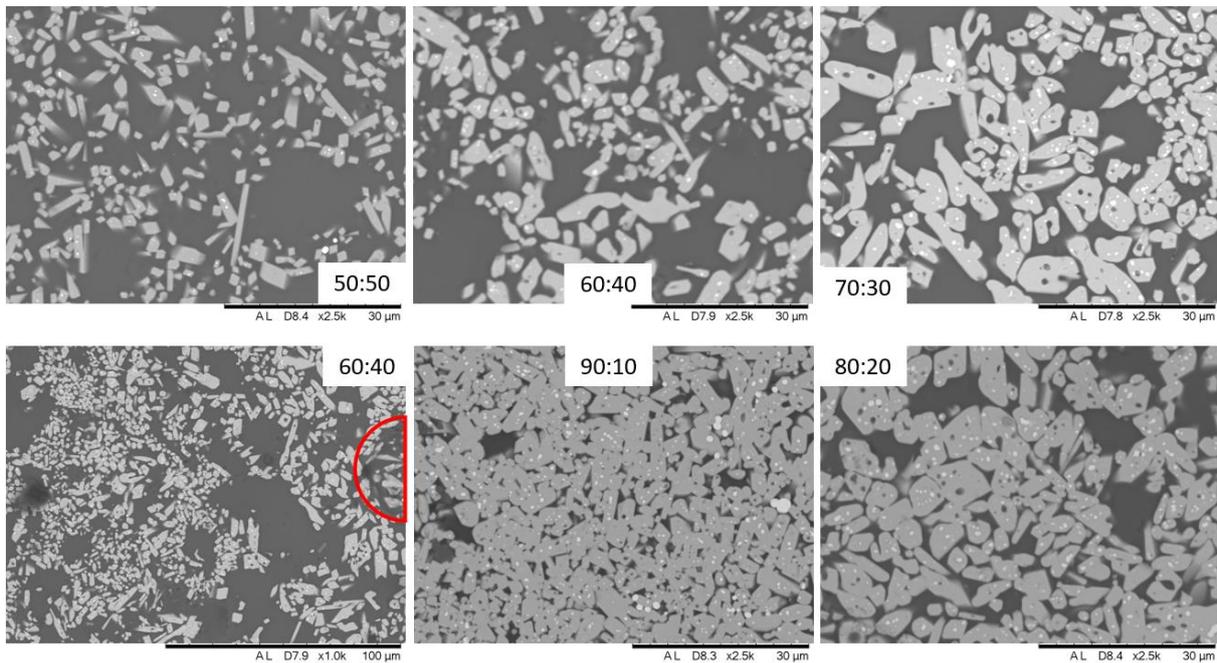


Figure 1. SEM micrographs of UTi_2O_6 glass-ceramics with different ceramic:glass ratios, as indicated. The white phase is UO_2 , light grey is UTi_2O_6 , and dark grey is glass. Note that the bottom left image is at a different magnification, and has a large region of porosity (as indicated in red).

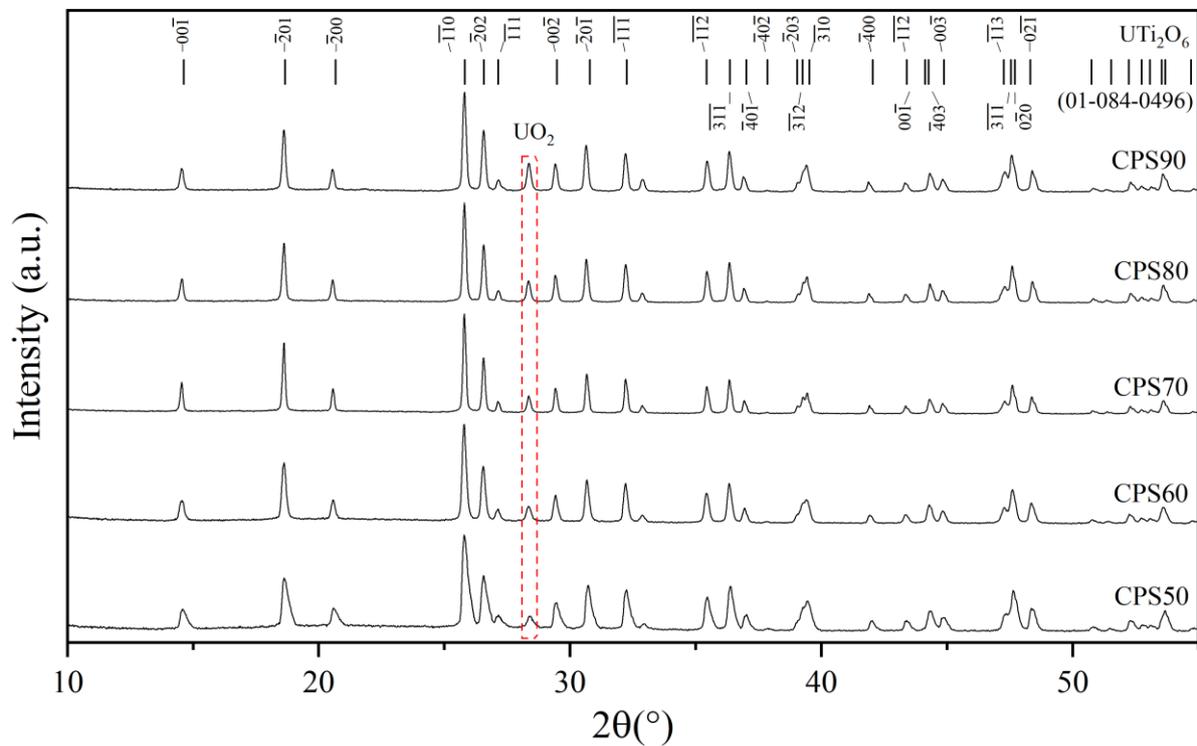


Figure 2. XRD patterns of CPS brannerite glass-ceramics with differing ceramic:glass ratio. The ceramic:glass ratio of each pattern is indicated, and the reflections of UTi_2O_6 are marked at the top.

3.2. HIPed brannerite glass-ceramic composites

Three HIP samples were prepared, one at 1100 °C and two at 1200 °C. The first sample, HIP1200a has the same composition as the sample CPS50, and was also processed at 1200 °C (however it was only heated at 1200 °C for four hours, rather than the 12 hours of the CPS samples). The main phases observed by XRD and SEM are brannerite and UO_2 ; however, the relative amount of UO_2 is higher (approximately 5% by weight) than that of the sample CPS50 (see Figure 3). As mentioned above, previous reports have shown that hyperstoichiometric amounts of TiO_2 can be necessary to prevent formation of free UO_2 , so sample HIP1200b was batched from the same precursors as HIP1200a but with the addition of a further 2.5 wgt% TiO_2 prior to the final homogenisation step. The phases observed by XRD and SEM match those of HIP1200a; however, the addition of excess TiO_2 reduced the relative amount of UO_2 in the phase assemblage. A small peak assignable to TiO_2 , rutile, is also observed, suggesting that addition of further TiO_2 would not cause complete reaction of the UO_2 .

The sample HIP1100 was made to investigate if the temperature of reaction could be further reduced (with a corresponding increase of the time at temperature to encourage full reaction) whilst still producing a high brannerite fraction glass-ceramic composite. The phase assemblage as observed by XRD and SEM consists of brannerite and UO_2 , the same as the samples processed at 1200 °C; however, the relative amount of UO_2 is evidently higher than for all other samples.

It is unclear why more UO_2 is observed in the HIPed samples when compared to CPS samples of the same composition. A possible explanation is offered by a report that the brannerite structure is unstable in reducing conditions

[5], such as those exerted by the stainless steel HIP canister. This is supported by the observation of higher amounts of unreacted UO_2 at the can-sample interface in the HIPed samples. However, samples of pure ceramic UTi_2O_6 have been formed under reducing atmospheres (24 hours at 1350 °C in 5% H_2 /95% N_2 atmosphere, unpublished work), so this may not offer a complete explanation of the phenomenon.

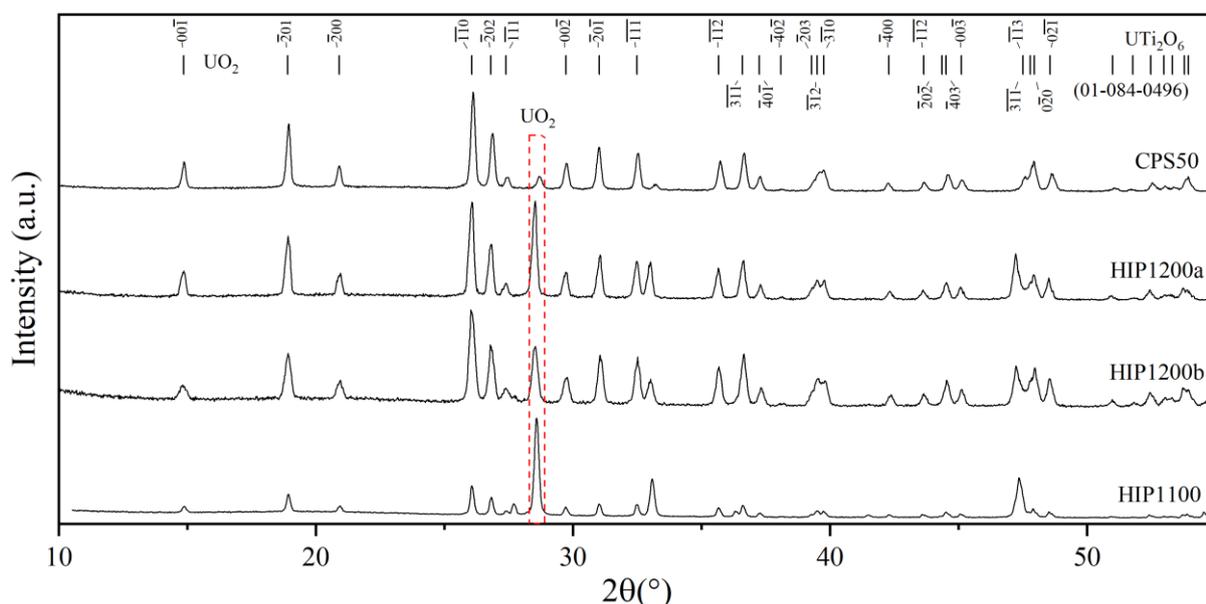


Figure 3. XRD patterns of brannerite glass-ceramics HIPed under different conditions. The conditions of each HIP sample are indicated and the reflections of UTi_2O_6 are marked at the top.

4. Conclusion

A range of UTi_2O_6 glass-ceramic composites have been synthesised, with a focus on investigating the effect of the glass:ceramic ratio on the temperature of formation of brannerite. When processed via a

CPS route at 1200 °C, UTi_2O_6 formed as the major crystalline phase for glass:ceramic ratios from 50:50 to 10:90, with UO_2 as a secondary product. When HIPed at 1200 °C, brannerite is still the majority product; however, the relative amount of UO_2 increases when compared to a CPS sample of the same as-batched composition. The mechanism causing this is not clear. When the temperature of reaction is further reduced to 1100 °C, significantly less brannerite is formed, with a much higher proportion of UO_2 observed in the final product.

As expected from the synthesis of brannerite glass-ceramic composites in the literature, UTi_2O_6 forms well in glass at 1200 °C, below the temperatures required for synthesis of a full ceramic from component oxides. Further work required to fully understand the extent and exact cause (although it is most likely caused by the glass phase lowering the barrier to diffusion of the ceramic phase reactants) of this effect is ongoing, with a focus on in-situ high temperature diffraction techniques.

5. References

- [1] Lumpkin G R, Leung S H F and Ferenczy J 2012 *Chem. Geol.* **291** 55.
- [2] Bailey D J, Stennett M C and Hyatt N C 2016 *Procedia Chem.* **21** 371.
- [3] Bailey D J, Stennett M C and Hyatt N C 2017 *MRS Adv.* **2** 557.
- [4] James M, Carter M L and Watson J N 2003 *J. Solid State Chem.* **174** 329.
- [5] Vance E R, Watson J N, Carter M L, Day R A and Begg B D 2001 *J. Am. Ceram. Soc.* **84** 141.
- [6] Zhang Y, Kong L, Karatchevtseva I, Aughterson R D, Gregg D J and Triani G 2017 *J. Am. Ceram. Soc.* **100** 4341.
- [7] Zhang Y, Karatchevtseva I, Kong L, Wei T and Zhang Z 2018 *J. Am. Ceram. Soc.* **101** 5219.
- [8] Zhang Y, Wei T, Zhang Z, Kong L, Dayal P and Gregg D J 2019 *J. Am. Ceram. Soc.* **102** 7699.
- [9] Dixon Wilkins M C, Stennett M C and Hyatt N C 2019 *MRS Adv.* in press.
- [10] Stennett M C, Freeman C L, Gandy A S and Hyatt N C 2012 *J. Solid State Chem.* **192** 172.

Acknowledgment

This research was sponsored in part by EPSRC under grant references EP/N017870/1, EP/S011935/1 and EP/S01019X/1. MCDW is grateful to EPSRC and NDA for provision of a doctoral training award. This research utilised the HADES / MIDAS Facility, established with financial support from the UK Department for Business, Energy and Industrial Strategy and EPSRC under grant reference EP/T011424/1.