Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 21 (2016) 371 – 377

Procedia Chemistry

5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

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

D. J. Bailey[a]*, M. C. Stennett[a] & N. C. Hyatt[a]

[a]*Immobilisation Science Laboratory, Department of Materials Science and Engineering, University of Sheffield, Sheffield, S1 3JD, United Kingdom*

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 wasteforms; 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 wasteform. 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.

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: Brannerite, X-ray diffraction, nuclear waste immobilization, mixed oxide fuel

* Corresponding author. Tel.:+44 (0) 1142 225973.
E-mail address: dbailey2@sheffield.ac.uk

Peer-review under responsibility of the organizing committee of ATALANTE 2016
doi:10.1016/j.proche.2016.10.052

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 [(1)]. 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 [(2,3)]. 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[(4,5)].

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) [(6–8)].

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 [(7,8)].

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 Kβ 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 μm). Samples were sputter coated with carbon to reduce surface charging effects.