



Full Length Article

Preparation of cerium titanate brannerite by solution combustion, and phase transformation during heat treatment



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ARTICLE INFO

Article history:

Received 26 October 2016
 Received in revised form 11 January 2017
 Accepted 11 January 2017
 Available online 18 January 2017

Keywords:

Cerium titanate
 Brannerite
 Chemical synthesis
 Crystal structure

ABSTRACT

An aqueous solution route was employed to prepare cerium titanate oxide brannerite. Thermal analysis, X-ray diffraction, Raman spectroscopy, transmission and scanning electron spectroscopy, were used to investigate the brannerite structure formation and bulk properties. Mixed metal oxides (TiO_2 , CeO_2 and brannerite CeTi_2O_6) were formed upon calcination at 800°C for 12 h. The amount of brannerite phase decreased to form the constituent oxides with increasing calcination temperature and only pure TiO_2 and CeO_2 were present after 1200°C calcination. The brannerite CeTi_2O_6 phase reformed at 1300°C , and its relative amount was increased with dwell time. After 48 h calcination at 1300°C , brannerite with only minor metal oxide impurities ($<1\%$) was observed. The sample melted at 1400°C which led to the collapse of brannerite back to its constituent oxides. Further, the phase formation was influenced by pelletization of the powders, which may be explained by a molar volume increase during brannerite formation. Attempts to confirm this hypothesis using Pu brannerite were inconclusive.

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1. Introduction

Cerium titanates including the brannerite phase have many important applications such as materials for photocatalysis, ferroelectrics, anti-reflective coatings, electrochromic layers, self-cleaning glasses and as chemical-mechanical polishing materials [1–6]. In particular, titanate ceramics with compositions MTi_2O_6 (where $M = \text{U}, \text{Th}, \text{Pu}$) are important actinide host matrices for the immobilization of actinide-bearing radioactive waste from nuclear power plants and weapons programs, with subsequent storage of the waste form in a geological repository [7]. Even though brannerite is a minor phase in Synroc type pyrochlore-rich waste forms, the pure end-member composition (UTi_2O_6) contains 62.8 wt.% UO_2 . Therefore, it can account for a significant fraction of the total amount of actinides in the bulk solid [7]. Since the ionic radius, coordination environment, and oxidation state of Ce ($3+/4+$) are similar to those of U ($4+$) and Pu ($3+/4+$), Ce is considered as an actinide “simulant” for U and Pu in the development of waste forms for the immobilization of high-level radioactive waste [7–15]. As a result, in this field the Ce analogue (CeTi_2O_6) has been studied extensively to simulate actinide brannerites MTi_2O_6 [7–15].

The brannerite crystal structure belongs to the monoclinic crystal system, with space group $C2/m$ and comprises infinite sheets of anatase-like corner and edge sharing TiO_6 octahedra which form layers in the ab plane. These layers are linked along the c -axis by MO_6 octahedra [16]. Due to the high thermodynamic stability of ceria and titania, no stable solid solution or reaction compound forms in an oxidizing atmosphere below 1300°C when mixing TiO_2 and CeO_2 [17]. However, when heated in the presence of an oxidizing agent or even gaseous oxygen from the air, CeO_2 and two moles of TiO_2 potentially form CeTi_2O_6 brannerite, which is reported to be stable between 1300 and 1350°C [17,18].

The commonly used method to produce cerium brannerite is by the mixed-oxide route [8–15]. This conventional solid-state reaction traditionally used for the preparation of these materials involves laborious heating cycles at 1350°C for over 96 h with repeated grinding of the component oxides to allow interdiffusion of the cations [8,9,13]. However, when the chemical reaction was undertaken at a molecular level using sol-gel or coprecipitation processing, the metastable compound $\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (corresponding to $\text{CeTi}_{2.33}\text{O}_{6.67}$) with a monoclinic brannerite structure was observed at relatively low air calcination temperatures (800 – 950°C) after a relatively short period of time [19–23], even though the structure was not fully crystallized. Further evolution of the ceria-titania solid solution at temperatures $>950^\circ\text{C}$ was not pursued in these studies [19–23].

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In the present study, we report a simple solution combustion method for the preparation of cerium brannerite powder using an aqueous medium and employing titanium(IV) bis(ammonium lactato)dihydroxide solution (Tyzor LA) and Ce(IV) salt as starting materials. As a consequence of this precursor selection, no complexing agent and/or polymerization agent are required, contrary to traditional sol-gel method. The mixing between Ce(IV) and Ti(IV) precursors in an aqueous medium is at a molecular level which ensures a uniform reaction between the two components. As a result, no milling procedure is needed and this simplifies the processing compared with a conventional mixed-oxide route. This study reports on the structural evolution of the powders and pellets following various heat treatments, as well as the densification of the pelletized powders.

2. Experimental procedure

2.1. Materials and method

Tyzor[®] LA, titanium(IV) bis(ammonium lactato)dihydroxide solution (50 wt.% in water), and ammonium cerium(IV) nitrate (98.5%+) were purchased from Aldrich and used as received. Milli-Q water was used in all experimental procedures. The titanium content in Tyzor LA was quantitatively determined by gravimetric analysis with standard deviation (σ) $\leq 1.0\%$. For a typical synthesis, the calculated mole ratios of Tyzor LA solution and ammonium cerium(IV) nitrate were dissolved in water to form a solution upon stirring. The solution was dried overnight at 80 °C in an oven and subsequently calcined in a furnace in air under various conditions.

When ammonium cerium(IV) nitrate is dissolved in water, $[\text{Ce}(\text{NO}_3)_6]^{2-}$ is formed; whereas Tyzor LA is in the form of $[\text{Ti-precursor}]^{2-}$ in aqueous solution. After drying and subsequent air calcination (with very slow ramp rate) in the temperature range of 700–1400 °C, various phenomena were observed including phase changes and melting.

2.2. Characterization

Thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric analysis (DTG) up to 1500 °C of 60 mg of dried powder (800 °C for 4 h) were performed in air with a heating rate of 5 °C min⁻¹ using a SETARAM TAG 24 (Caluire, France) apparatus with a normal gas flow-rate of 25 cm³ min⁻¹. After dwelling at 1500 °C for 1 min, the temperature was decreased to 200 °C at a rate of 5 °C min⁻¹. A platinum crucible was used for the experiment and aluminum oxide was used as reference material.

Raman spectra were collected using a Renishaw inVia Raman spectrometer equipped with an Argon ion laser (514 nm) and a Peltier cooled charge-coupled device (CCD) detector (Renishaw plc, Old Town, Gloucestershire, UK) at room temperature. Stokes shifted Raman spectra were collected in the static mode in the range of ~ 100 –1000 cm⁻¹ with a spectral resolution of 1.7 cm⁻¹ for the 1800 l/mm grating. The spot size was around 1.5 μm for 50 \times magnification.

X-ray diffraction patterns were measured using a BRUKER D8 instrument, with weighted $\text{CuK}\alpha$ radiation, in an angular range of 5–120° (2 θ), with a step size of 0.02° and an acquisition time of 5 s per step. Unit cell refinements were carried out by the Le Bail method [24] using the RIETICA program (version 1.7.7) [25]. The peak profiles were approximated by the Pseudo-Voigt function. The lattice parameters were refined with the gradual addition of parameters and continuous graphical modeling of the background until the *R* factors ceased to change.

A JEOL JEM 2010F (JEOL Ltd., Akishima, Tokyo, Japan) transmission electron microscope (TEM), equipped with a field emission

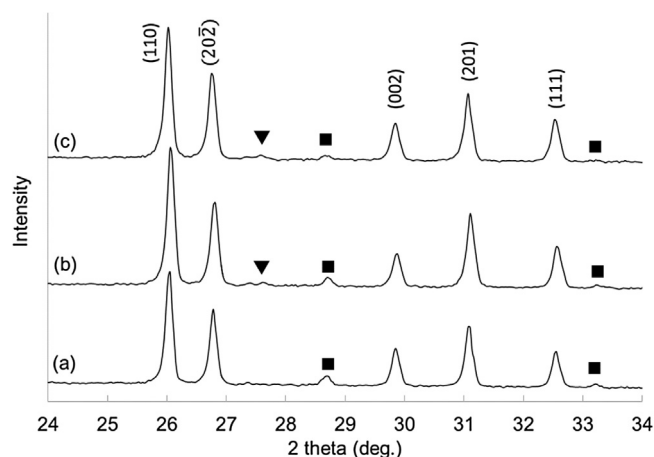


Fig. 1. XRD pattern of powder samples calcined at 1300 °C for 48 h. (a) CeTi_2 , (b) $\text{CeTi}_{2.05}$, (c) $\text{CeTi}_{2.1}$. (▼): rutile-type TiO_2 ; (■): CeO_2 .

gun (FEG) electron source operated at 200 kV, was used to record selected area electron diffraction patterns (SAED). TEM images were recorded with a CCD camera mounted in the 35 mm port above the TEM viewing chamber (Model 782, Gatan, Pleasanton, CA). Samples for TEM were prepared by suspending powder in ethanol and depositing several drops onto a carbon coated 200-mesh copper grid. The phase-composition of samples was analyzed by energy dispersive spectra (EDS), using calculated *k*-factors and library spectra for spectrum fitting.

Scanning electron microscopy (SEM) was used to analyze the microstructure and phase-composition of sintered samples via energy dispersive spectra (EDS). Samples were examined in a Zeiss Ultra Plus scanning electron microscope (Carl Zeiss NTS GmbH, Oberkochen, Germany) operating at 15 kV equipped with an Oxford Instruments X-Max 80 mm² SDD X-ray microanalysis system. Samples were mounted in an epoxy resin and polished to 1 μm diamond finish. A thin carbon film (~ 5 nm) was deposited onto the polished surface. Semi-quantitative analysis was performed on the Oxford Instruments INCA software. A copper metal standard was used for the Quant Optimization to ensure the best fit of the stored profiles within the software. The analytical errors due to spectrum processing are approximately 0.4 and 0.2 wt.% for Ti and Ce respectively, leading to an error of $\sim 1\%$ in the formulation unit.

For density determination, the powder calcined at different temperatures was pelletized using a uniaxial press at approximately 180 MPa, followed by sintering at 1300 °C for 48 h in air. Archimedes' displacement method in distilled water was used to measure the bulk density of the pellet sample. Theoretical density was calculated from unit cell parameters obtained following Le Bail refinement of XRD data.

3. Results and discussion

3.1. Powder samples

In order to produce single phase CeTi_2O_6 , powder samples were synthesized with stoichiometries $\text{CeTi}_{2.0}$, $\text{CeTi}_{2.05}$, and $\text{CeTi}_{2.1}$ and these were calcined at 1300 °C for 48 h and analyzed by XRD (Fig. 1). The results showed that the amount of CeO_2 decreases with increasing Ti:Ce mole ratio from 2.0 to 2.1. The $\text{CeTi}_{2.1}$ sample was the closest system to form single phase CeTi_2O_6 , which is in good agreement with recent work describing the formation of single phase brannerite $\text{Ce}_{0.975}\text{Ti}_2\text{O}_{5.95}$ [9]. Further, the presence of trace CeO_2 and TiO_2 in the $\text{CeTi}_{2.1}$ sample suggest incomplete reaction under the current calcination conditions. However, the $\text{CeTi}_{2.1}$ system was selected for all subsequent investigations.

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