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Phase evolution and microstructure analysis of $CaZrTi_2O_7$ zirconolite in glass

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ABSTRACT

The internal crystallization of $CaZrTi_2O_7$ zirconolite in a sodium alumino-borosilicate glass has been investigated with powder X-ray diffraction (XRD), scanning electron microscopy and energy dispersion spectroscopy (SEM-EDS), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) techniques. The samples have been prepared using a soft chemistry route and ceramic phase evolution has been observed with sintering time. Zirconolite as the dominant phase at 1 h sintering gradually changes to baddeleyite structured materials for longer sintering times. XRD shows that one dominant phase belongs to zirconolite at 3 h sintering, however, SEM-EDS reveals that the dominant ceramic phase is actually baddeleyite phase, which is enclosed by zirconolite phase. TEM and SAED patterns also confirm the crystallization of zirconolite phase in glass. The addition of CaO enhances the formation of zirconolite (i.e. impedes baddeleyite phase) with CaO to glass weight ratio $\leq$ 35:100.

1. Introduction

A glass-ceramic system, which combines the advantages of both ceramic and glass, has attracted recent attention as one of the potential nuclear waste forms for the immobilization of actinide-rich radioactive wastes [1–7]. The crystalline phases are able to host actinides into their stable crystal structures while the residual glass acts as a secondary barrier for the radioactive elements incorporated in the crystalline material as well as a versatile matrix to accommodate processing chemicals and impurities in the actinide-rich waste streams.

Zirconolite ($CaZrTi_2O_7$) is one of the major compositions in Synroc (synthetic rock) formulation composed of zirconolite, pyrochlore, perovskite, hollandite and rutile structured phases [8–10]. The monoclinic structure of $CaZrTi_2O_7$ is formed by stacking of layers of edge-shared TiO_6 octahedra, TiO_5 trigonal pyramids and layers of Ca^{2+} and Zr^{4+} ions. This particular crystal structure is able to accommodate metal ions having widely different oxidation states and ionic radii and also can crystallize in a number of polytypes without significantly changing its structural framework. As a result, the zirconolite-related structures are promising to accommodate larger proportion of actinides and possessing properties such as higher leaching resistance, higher chemical durability and radiation tolerance [8–10].

Zirconolite based glass ceramics (GCs) have been developed as potential waste forms for the immobilization of nuclear wastes, especially the actinide residue wastes, and also have potential for the immobilization of separated minor actinides [1–4]. However, unlike lanthanide titanate pyrochlores ($Ln_2Ti_2O_7$) which can be internally crystallized inside a glass matrix [11,12], the formation of zirconolite phases inside a glass matrix is much more complicated [13–23]. One of the reasons is that zirconolite is thermodynamically instable, especially in a higher silica content glass [4,7]. In a two-step thermal synthesis [13–23], zirconolite glass-ceramic is produced by melting an oxide mixture (the parent glass) at elevated temperatures ($\geq$ 1500 °C), then submitting it to a heat treatment (annealing) at lower temperatures (~ 800 to 1500 °C) to evaluate the degree of zirconolite crystallization. Neodymium is used as an actinide surrogate. In a one-step synthesis [4,7], ceramic and glass components are mixed together in one-pot and the GC samples are prepared. However, an intermediate hot isostatic pressing (HIP) stage is normally utilized to fabricate physically integrated large samples. Maddrell et al. [7] have revealed that the formation of crystalline phases in GC waste forms is dependent on the composition of the glass matrix. Zirconolite forms as the sole crystalline phase only for the most aluminous glass, that is, $NaAlSi_3O_8$. Thermodynamically, zirconolite becomes the preferred crystalline phase at low silica activities. In a separate work [4], the authors have used the same glass to study the evolution of crystalline phases as a function of temperature (1000–1200 °C) and time (30–90 min). The work has shown that perovskite and sphene form as transient phases before the formation of zirconolite as the final crystalline phase at 1200 °C. HIPing process has been used to prepare low porosity samples while cold

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pressed powder is too porous for microstructure analyses using micrographic imaging [4].

In the present work, a soft chemistry approach is used to prepare the ceramic phase to promote the intimate reaction of the ceramic components and the homogeneity of the product. The mixture of ceramic and glass precursor powder ($NaAl_{0.8}B_{0.2}Si_3O_8$) is cold pressed and sintered pressurelessly at 1250 °C in air for 1–16 h, in order to investigate the effect of long time sintering on ceramic phase equilibrium in glass. XRD is used to analyze the crystalline phases of the bulk materials, whereas SEM-EDS and HRTEM-SAED are utilized to investigate the microstructures of the ceramic phases. The results reveal that the combination of both the bulk material and the microstructure analysis techniques lead to a much better understanding of zirconolite phase evolution in a glass matrix. The effect of CaO addition on the formation of crystalline phases is also investigated. The formation of zirconolite phase is enhanced by addition of CaO in glass.

2. Experimental procedure

2.1. Materials and method

Tyzor® LA, titanium(IV) bis(ammonium lactato)dihydroxide solution (50 wt% in water), calcium(II) nitrate tetrahydrate (99%+), sodium carbonate (99.5%+), aluminum oxide (99.5%+), boric acid (99.5%+), silicon dioxide (99.9%+) were purchased from Sigma-Aldrich; zirconium(IV) nitrate pentahydrate was purchased from Fluka 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.

Glass (formula as $NaAl_{0.8}B_{0.2}Si_3O_8$) precursor powder was prepared by mixing calculated amounts of Na_2CO_3, Al_2O_3, H_3BO_3, and SiO_2 with designed molar ratios, and heat treated in a furnace in air at 550 °C for 3 h. The oxide compositions were calculated to be Na_2O (11.97 wt%), Al_2O_3 (15.75 wt%), B_2O_3 (2.69 wt%), and SiO_2 (69.60 wt%).

For a typical synthesis, 10 mmol of Tyzor LA (an aqueous solution) was weighed in a 100 mL round alumina crucible, 50 mL of water was added. 5 mmol of calcium nitrate and 5 mmol of zirconium nitrate were mixed thoroughly with the above aqueous solution. A clear aqueous solution was formed upon stirring, which was dried in an oven at 90 °C overnight. The dried product was heated in a furnace in air at 550 °C for 6 h, with temperature ramp rate of 2 °C/min. The majority of the organic species were removed upon heat treatment and a metal-composite ($CaZrTi_2$-oxide) in a powder form was produced, with light yellow pale color.

The composite powder was calcined at 1250 °C for 15 h followed by XRD analysis to confirm the formation of zirconolite. For GC sample preparations, the equal weight of glass precursor powder (0.500 g) and composite powder (0.500 g), both being heated at 550 °C, were thoroughly mixed, pelletized using a uniaxial press at approximately 180 MPa, followed by sintering at 1250 °C for different times in air, with heating rate at 3 °C/min and cooling rate at 10 °C/min. The pelletized glass-ceramic samples were termed as GC samples.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands) with Cu K_α radiation ($\lambda = 1.5418$ Å) at 45 kV and 40 mA. XRD data were obtained using an angular range of 10–65° two theta in a continuous mode with a step size of 0.02° (2θ) with an acquisition time of 2 s per step. GC samples were finely ground manually before analyzing.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze the microstructures and phase compositions. 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 mm^2 SDD X-ray microanalysis system. For pelletized samples, they were cut and mounted in an epoxy resin (with cross section on top) 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.

Transmission electron microscopy (TEM) investigation was performed on a JEOL 2200FS (JEOL Ltd., Akishima, Tokyo, Japan) instrument, equipped with a field emission gun (FEG) electron source operated at 200 kV to record selected area electron diffraction patterns (SAED). The phase composition of samples was analyzed by energy dispersive X-ray spectrometry (EDS) under TEM using an Oxford Instruments® EDS detector. The specimens were prepared by finely grinding GC sample, suspending the ground powder in ethanol and depositing several drops onto a carbon coated 100-mesh copper grid.

3. Results and discussion

3.1. XRD analysis

Calcination temperature for fabricating GC samples is critical considering the factors including formation of the desired ceramic phase in glass, minimization of the impurities (undesired minor ceramic phases), glass melting and evaporation, and production cost, etc. A significant amount of zircon ($ZrSiO_4$) is present in a GC pelletized sample sintered at 1200 °C for 3 h (data not shown) in this work. As a result, 1250 °C is used in subsequent studies. Higher temperatures are not practical considering the production cost, the evaporation of glass phase and its melting. To confirm the formation of zirconolite at 1250 °C, the ($CaZrTi_2$-oxide) composite, which has been heated at 550 °C for 6 h, is calcined at 1250 °C for 15 h. The XRD peaks with Miller indices in Fig. 1 confirm the zirconolite-2M crystal structure [19]. Almost phase pure zirconolite-2M (monoclinic polytype) is produced at this processing condition. XRD patterns of CaO, ZrO_2, and TiO_2 powders calcined at 1300 °C for 6 h are shown in Fig. S1 with the intense peaks for CaO ($2\theta = 27.6, 36.2, 54.5°$), ZrO_2 ($2\theta = 28.2, 31.5°$) and TiO_2 ($2\theta = 32.3, 37.5, 53.9°$). No single metal oxides are observed in zirconolite powder (Fig. 1) suggesting that the ceramic components are completely reacted.

Fig. 2 shows the XRD patterns of GC samples calcined at 1250 °C for 1–15 h. The main diagnostic peaks for each phase indicate that samples contain zirconolite ($CaZrTi_2O_7$), zircon ($ZrSiO_4$); baddeleyite structured materials (ZrO_2 and/or $Zr_xTi_{1-x}O_2$ with $x \geq 0.5$); perovskite ($CaTiO_3$) and rutile (TiO_2), mainly Synroc phases. Small amount of sphene ($CaTiSiO_5$) ($2\theta = 29.8$) is observed especially at shorter sintering times. Fig. S2 displays the XRD patterns of corresponding minerals derived from open source, which clearly show the major peak positions and the relative intensities for each mineral. The XRD data show that in all

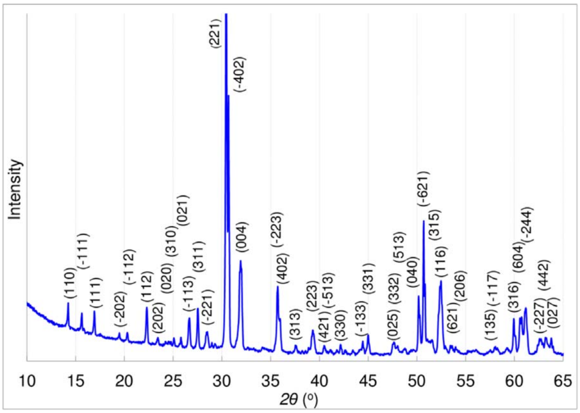

Fig. 1. XRD pattern of $CaZrTi_2O_7$ powder sample calcined at 1250 °C for 15 h.