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Preparation and characterization of borosilicate glass-ceramics containing zirconolite and titanite crystalline phases

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ABSTRACT

$CaCO_3$, $ZrSiO_4$, and TiO_2 (abbreviated as CZST) in the stoichiometric mole ratio (2:1:3) were added to borosilicate system. Borosilicate glass-ceramics containing zirconolite and titanite crystalline phases were prepared by controlled crystallization of the parent glass. The effects of CZST addition (10, 20, 30, and 40 wt.%) on crystalline phases, microstructure, and chemical durability of the glass-ceramics were mainly investigated. The results show that the samples possess the amorphous structure when the concentration of CZST is lower than 30 wt.%. For the glass-ceramics with 30 wt.% CZST (GC-30) heated at 740 °C for 2 h, only the zirconolite-2M phase was observed. For the sample with 40 wt.% CZST (GC-40) heated at 810 °C for 2 h, the major crystalline phases are $CaZrTi_2O_7$ and $CaTiSiO_5$. In addition, the grains of the $CaZrTi_2O_7$ and $CaTiSiO_5$ show a dendritic and columnar shape, respectively. The static leaching test shows that the normalized mass loss (NL_i) for B, Si, and Na of the sample GC-30 remains almost unchanged ($\sim 10^{-3}$ g/m^2) after 14 days. Compared to the borosilicate glass, the GC-30 possesses particularly the lower values of the NL_i for B and Na. These results indicate that the borosilicate glass-ceramics containing zirconolite and/or titanite crystalline phases have the potential as host materials for actinide-rich high level radioactive wastes.

1. Introduction

Borosilicate glass has long been the first choice of material for the immobilization of high level radioactive wastes (HLW) due to its good glass-forming ability, chemical durability, radiation stability, etc. However, there is a potential risk that the conventional borosilicate glass waste forms partially crystallize either during annealing, or during long-term storage in deep geological environment. Usually, this crystallization proceeds in an uncontrolled manner, leading to the formation of undesirable stresses that may cause the glass to crack. Consequently, leaching rates of nuclides in the glass waste forms may be significantly enhanced [1]. On the other hand, it must be noted that the solubility of actinide elements in the borosilicate glass is relatively low, i.e. <3 wt.% [1–3]. This may act as "waste load" limiting factor for the immobilization of actinide-rich HLW.

Glass-ceramics containing highly durable crystalline particles homogeneously dispersed in the bulk of a glass matrix have been proposed as important candidates for the immobilization of HLW [1,4–6]. Zirconolite ($CaZrTi_2O_7$)-based glass-ceramics are of considerable interest, especially in the area of minor actinides and lanthanides [7–10], because zirconolite is well known for its excellent capacity to incorporate actinides and lanthanides ions into the Ca and Zr sites of its structure [11]. Loiseau et al. [7,8] studied bulk and surface crystallization processes in calcium aluminosilicate (SiO_2–Al_2O_3–CaO–TiO_2–ZrO_2) parent glasses. It was found that zirconolite was the only crystalline phase to crystallize in the bulk of the glass [7]. Interestingly, a thin partially crystallized layer containing titanite and anorthite (nominally $CaTiSiO_5$ and $CaAl_2Si_2O_8$, respectively) growing from glass surface was also observed after heat treatment in the range of 1050–1200 °C. Titanite is the only crystalline phase in the layer able to incorporate significant quantities of trivalent lanthanide ions in the Ca site of its structure [8]. As titanite is a common constituent of many types of rocks which show excellent long-term stability in geological environment. Titanite-based glass-ceramics (SiO_2–Al_2O_3–CaO–Na_2O–TiO_2) have already been proposed for the immobilization of Canadian deuterium uranium (CANDU) fuel wastes [12]. Thus, titanite crystalline phase is favorable in the zirconolite-based glass-ceramics for the immobilization of actinides.

However, the melting temperatures of the calcium aluminosilicate glass are relatively high (~1550 °C). For relatively long crystal growth durations (2–300 h) at high temperature (1050–1200 °C), zirconolite is not thermodynamically stable in the calcium aluminosilicate glass-ceramics system. The growth of other crystalline phases (e.g., titanite, anorthite, baddeleyite, wollastonite, etc.) from the surface progressively consumes the zirconolite crystals of the bulk [8]. Consequently, in order to reduce the risks of progression of the other unfavorable crystals from the surface towards the bulk of the glass-ceramics at the expense of zirconolite, the crystal growth temperature must be not too high and/

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or the heating duration at this temperature must not exceed a few hours.

Recently, Mahmoudysepehr et al. [13] developed a new zirconolite-based glass-ceramic belonging to the SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) system. The addition of PbO, B_2O_3 and K_2O was used to reduce the liquidus temperature and promote the dissolution of ZrO_2 in the glass. Although the glass-ceramic containing 34 wt. % of monoclinic zirconolite can be prepared after heating at 770 °C for 4 h, the melting temperatures are still relatively high (1420–1470 °C). This would cause an additional problem of the serious evaporation of PbO during the melting process.

According to our previous work [14], the synroc which consists of zirconolite and titanite crystalline phases can be obtained in the range of 1230–1260 °C by solid-state reaction method using $CaCO_3$, $ZrSiO_4$, and TiO_2 as raw materials. The molar ratio of $CaCO_3$ to $ZrSiO_4$ to TiO_2 is 2:1:3. In this work, $CaCO_3$, $ZrSiO_4$, and TiO_2 (abbreviated as CZST) in the stoichiometric ratio (2:1:3) were added to the borosilicate system. It was expected that zirconolite and titanite crystalline phases could form in the borosilicate glass by controlled cooling of the corresponding melt. The effects of CZST addition on the crystalline phases, microstructure, and chemical durability of borosilicate glass-ceramics were mainly investigated. The related crystallization mechanism of the glass-ceramics was also discussed.

2. Experimental procedures

The borosilicate glasses were prepared with the following levels (wt. %): SiO_2 (45.0), B_2O_3 (20.0), Al_2O_3 (6.0), Na_2O (12.0), and other additives (17.0). This composition was selected because it was reported to have good chemical durability and relatively low melting temperature (~1150 °C) [15]. CZST with different concentrations (10, 20, 30, and 40 wt. %) were added to the borosilicate system. The oxide or carbonate powders of the above compositions were calcined at 850 °C for 1 h to dissociate carbonates. They were then melted at 1150–1200 °C for 2 h in high alumina crucibles. All glass melts were stirred with a platinum stirrer for 1 h after reaching the maximum temperature. Then the heat treatment was performed at temperatures between 730 °C and 900 °C for 2 h in an electric furnace to form glass-ceramics.

The glass-ceramic samples were ground in an agate mortar to pass a 100–200 mesh sieve. X-ray diffraction (XRD) characterization was performed using Cu Kα radiation (X' Pert PRO) to check the amorphous nature of the samples and to identify the crystalline phases. In order to determine the glass transformation temperature T_g and to study the glass crystallization behavior, differential thermal analysis (DTA) measurements were performed on samples under air with the help of a thermal analysis apparatus (SDT Q600). The heating rate was 20 °C min^{-1}. Glass-ceramic powders with two different particle size distributions (<50 and 75–150 μm) were used for the DTA studies. The bulk and surface of the glass-ceramics were observed using a scanning electron microscope (SEM, S400). The chemical durability of the glass and glass-ceramic samples was assessed by static leaching experiments (Product Consistency Test, PCT) at 90 °C with the 75–150 μm powder size fraction. Solution samples were taken at regular intervals (3, 7, 14, 28, 42 days) and analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500). Normalized mass loss for element (i) NL_i was calculated using the formula given below [16]:

$$NL_i = \frac{C_i \cdot V}{x_i \cdot S} \tag{1}$$

where C_i is the concentration of the element in the solution, x_i is the mass fraction of the element in the glass samples, S is the surface area of the glass-ceramic powders, and the V is the volume of the solution samples. The S/V ratio is about 2000 m^{-1}.

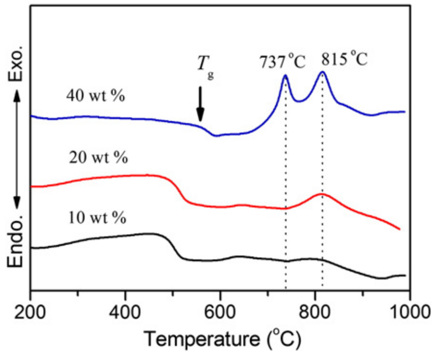

Fig. 1. DTA traces of samples with 10, 20, and 40 wt. % CZST in the temperature range of 200–1000 °C.

3. Results and discussion

Fig. 1 shows the DTA traces of the samples with 10, 20, and 40 wt. % CZST in the temperature range of 200–1000 °C. The T_g values which were determined by the DTA endothermic effect are about 470, 490, and 530 °C for the sample with 10, 20, and 40 wt. % CZST, respectively. Except for a small shift of peaks, the DTA curves of the samples with 10 and 20 wt. % CZST are very similar, and no obvious exothermic effect is detected during DTA runs (Fig. 1). For the sample with 40 wt. % CZST, two relatively sharp exothermic peaks are observed at about 737 and 815 °C, respectively. It is interesting to notice that a similar phenomenon has already been observed by Mahmoudysepehr et al. [13] for the SiO_2–PbO–CaO–ZrO_2–TiO_2–(B_2O_3–K_2O) system. A sharp exothermic peak at about 770 °C was observed for this lead silicate system, which was attributed to bulk crystallization of monoclinic zirconolite phase in the specimen. The other peak appearing at higher temperature (~860 °C) was wide and small in height so they did not consider this peak for further study. In the present work, it seems that the exothermic effect occurring at about 737 °C can also be attributed to zirconolite crystallization from the bulk of glass particles [7,13]. The other exothermic effect occurring at about 815 °C may be attributed to titanite crystallization from the surface of glass particles [7,8,17]. Additional experimental data will be provided below for further discussion.

Fig. 2 shows the XRD patterns of borosilicate glass and the samples with different concentration (10, 20, 30, and 40 wt. %) of CZST heated at 740 °C for 2 h. The sample with 40 wt. % CZST heated at 810 °C for 2 h is also shown in Fig. 2. For the borosilicate glass, a broad hump in between 20° and 35° is observed, which suggests its typical amorphous nature. Similar to the borosilicate glass, both of the samples with 10 and 20 wt. % CZST also have the amorphous structure. When the concentration of CZST increases to 30 wt. % (abbreviated to GC-30),

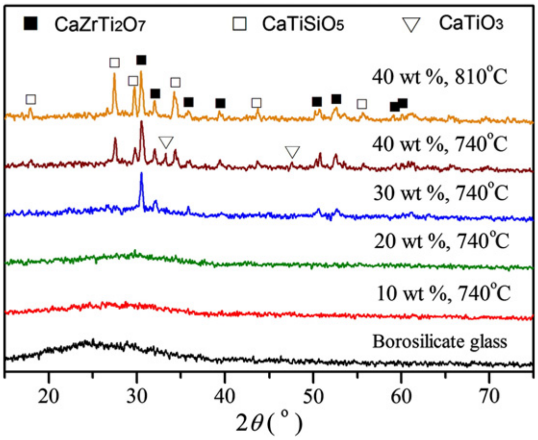

Fig. 2. XRD patterns of borosilicate glass and the samples with different concentrations of CZST heated at 740 °C and 810 °C for 2 h.