



Structure and chemical durability of barium borosilicate glass–ceramics containing zirconolite and titanite crystalline phases



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ABSTRACT

In order to increase the solubility of actinides in the glass matrix, the effects of CaO, TiO₂, and ZrSiO₄ addition (abbreviated as CTZ, in the mole ratio of 2:2:1) on crystalline phases, microstructure, and chemical durability of barium borosilicate glass–ceramics were investigated. The results show that the samples possess both zirconolite-2M and titanite phase when the CTZ content is greater than or equal to 45 wt.%. For the glass–ceramics with 45 wt.% CTZ (CTZ-45), only zirconolite-2M phase is observed after annealing at 680–740 °C for 2 h. The CTZ-45 possess zirconolite-2M and titanite phases after annealing at 700 °C first, and then annealing at 900–1050 °C for 2 h. Furthermore, the zirconolite-2M and titanite grains show a strip and brick shape, respectively. The CTZ-45 annealing at 950 °C shows the lower normalized leaching rates of B, Na and Nd when compared to that of CTZ-0 and CTZ-55.

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1. Introduction

High-level radioactive wastes (HLW) produced by spent fuel reprocessing containing fission products and actinides must be immobilized in highly durable solid matrices. Borosilicate glass has long been the first choice of material for the immobilization of HLW due to its good glass-forming ability, chemical durability, radiation stability, etc [1–3]. However, the solubility of actinides in borosilicate glass is very low. For instance, Eller et al. [4] reported the solubility limits of about 2 wt.% for oxides of Np, Pu and Am in borosilicate glass. Recently, Mishra et al. [5] reported that the addition of BaO can significantly improve the incorporation of actinide surrogates (Th⁴⁺) in borosilicate glass. The barium borosilicate glass can accommodate up to 15.86 wt.% of ThO₂ and about 7.5 wt.% of UO₃ [6,7]. Moreover, the incorporation of BaO as modifier in borosilicate matrix show marked improvement in enhancing the solubility of sulfate. This is very helpful to prevent formation of yellow phase in the glass matrix. Therefore, barium borosilicate glass is also potential matrix for immobilization of sulfate bearing HLW.

However, the glass is metastable in nature, which could induce

formation of uncontrolled crystalline phases during the long-term storage in deep geological repositories. Therefore, the applications of barium borosilicate glass might be limited significantly. Glass–ceramics containing highly durable crystalline particles homogeneously dispersed in the bulk of a glass matrix have also been proposed as important candidates for the immobilization of HLW (double containment principle) [8,9]. Zirconolite (CaZrTi₂O₇)-based glass–ceramics have attracted a great deal of interest, because it is well-known for its excellent capacity to incorporate actinides into Ca and Zr sites of its structure [8–13]. To date, there are only few reports on the barium borosilicate glass–ceramics containing zirconolite crystalline phases.

Our previous report [14] showed that only the zirconolite-2M phase could be obtained when borosilicate glass doped with a certain amount of CaCO₃, ZrSiO₄ and TiO₂. Nevertheless, BaO was not present in the glass composition. The aim of this work was to investigate the effects of the content of nucleating agents CaO, TiO₂, and ZrSiO₄ (the molar ratio of CaO to TiO₂ to ZrSiO₄ is 2:2:1, abbreviated as CTZ) on crystalline phases, microstructure, and chemical durability of the barium borosilicate glass–ceramics. A small amount of neodymium (~4 wt.%) was added to simulate the trivalent actinides in a waste form such as Am and Cm because they have similar charge and close ionic radii [for instance in 6-fold coordination: $r(\text{Cm}^{3+}) = 0.097 \text{ nm}$, $r(\text{Am}^{3+}) = 0.0975 \text{ nm}$, $r(\text{Nd}^{3+}) = 0.0983 \text{ nm}$] [12,15]. Generally speaking, thermal

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treatment temperatures have significant influence on the structure of glass–ceramics. So the effect of different thermal treatment temperatures on the crystalline phases and microstructure of the barium borosilicate glass–ceramics was also studied.

2. Experimental procedures

The glass and glass–ceramics compositions with different contents of nucleating agents were prepared using reagent grades of SiO₂, H₃BO₃, Na₂CO₃, BaCO₃, Nd₂O₃, CaCO₃, TiO₂ and ZrSiO₄. The detailed compositions are given in Table 1. Glass batches with desired compositions were mixed thoroughly in an agate mortar and calcined in an alumina crucible at 850 °C for 2 h to decompose carbonates, then melted at 1150–1250 °C for 3 h in the alumina crucible to form homogeneous melts using muffle furnace. The melt was controlled from melting temperatures to thermal treatment temperatures in the muffle furnace to prepare glass–ceramics.

In order to investigate different thermal treatment temperatures on the structure of the glass–ceramics, two methods were used in our experiment:

➤Method A (one step): the glass–ceramics were prepared at the annealing temperatures with 680 °C, 700 °C, 720 °C and 740 °C for 2 h, respectively, which are slightly higher than glass transformation temperature T_g [16].

➤Method B (two step): the glass–ceramics were annealing first at 700 °C for 2 h, and then annealing at different crystallization temperatures (900 °C, 950 °C, 1000 °C and 1050 °C) for 2 h.

Glasses were obtained by quenching the melts in cold water, and the quenched glasses were crushed and sieved to pass a 100–200 mesh sieve. The glass transformation temperatures and crystallization temperatures were determined by differential thermal analyses (DTA) with the help of a thermal analysis apparatus (SDT Q600) from room temperature to 1200 °C at a rate of 20 °C/min in air using approximately 10 mg glass powders. The bulk of glass–ceramics were pulverized into powder in an agate mortar for X-ray diffraction (XRD) using a X'Pert PRO Roentgen diffractometer system with Cu K α rays ($\lambda = 1.5418 \text{ \AA}$) analysis to investigate the amorphous nature and the crystalline phases of the samples. The microstructure of these samples was analyzed using a scanning electron microscope (SEM, S400) fitted with an energy-dispersive X-ray analyzer (EDX) accessory and optical microscope (4XC-PC). The slice specimens firstly were etched in 10 wt.% HF solution for 10–15 s and then rinsed with distilled water and sonicated to remove any debris, specimens were coated with a film of gold before the microstructure of samples was studied. The chemical durability of the glass and glass–ceramic samples was evaluated with the Product Consistency Test (PCT) [17] at $90 \pm 1.0 \text{ °C}$ in de-ionized water (pH = 7) within polytetrafluoroethylene reactors. The leaching powders were crushed, selected by sieving between 100 and 200 meshes, washed and dried. Solution

Table 1
Compositions of barium borosilicate glass and glass–ceramics (wt.%).

Specimen	SiO ₂	B ₂ O ₃	Na ₂ O	BaO	CaO	TiO ₂	ZrO ₂	Nd ₂ O ₃	T_g (°C)
CTZ-0	48.00	19.20	9.60	19.20	–	–	–	4	578
CTZ-20	38.00	15.20	7.60	15.20	5.68	8.09	6.24	4	604
CTZ-40	28.00	11.20	5.60	11.20	11.35	16.17	12.47	4	639
CTZ-45	25.50	10.20	5.10	10.20	12.77	18.19	14.03	4	648
CTZ-50	23.00	9.20	4.60	9.20	14.19	20.21	15.59	4	656
CTZ-55	20.50	8.20	4.10	8.20	15.61	22.24	17.15	4	663

Note: x in CTZ-x is the mass fraction of nucleating agents CaO, TiO₂ and ZrSiO₄ (the molar ratio is 2:2:1).

samples were replaced in the new demonized water at regular intervals (1, 3, 7, 14, 28, 42 days) and analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500) and inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x). The normalized leaching rate LR_i ($\text{g m}^{-2} \text{ d}^{-1}$) of element i was calculated using the formula given below [18]:

$$LR_i = \frac{C_i \cdot V}{f_i \cdot S \cdot \Delta t}$$

Where C_i is the concentration of element i in the solution (g/L), f_i is the mass fraction of the element in the glass and glass–ceramic samples, V is the volume of the leaching solution (L), S is the surface area of the sample (m^2), the value of S/V is about 2000 m^{-1} , Δt is the duration of the experiment in days.

3. Results and discussion

3.1. DTA analysis

Fig. 1 shows the DTA curves of the different glass specimens in the temperature range of 500–1100 °C. Both the glass specimens of CTZ-0 and CTZ-20 have similar DTA curves except for a weak exothermic peak around 975 °C. In addition, the slight endothermic effect around 750 °C becomes weak with the count of CTZ increases, which might be due to an endothermic surface process, and the height, width and temperature span of the endothermic peak depend upon the glass surface chemistry [19]. For the glass of CTZ-40, two relatively sharp exothermic peaks are observed at about 905 °C and 970 °C, respectively. In addition, the weak exothermic peak is also found at about 1030 °C. When the content of CTZ increases to 55 wt.%, three exothermic peaks are located at about 895 °C, 935 °C and 1035 °C, respectively. The DTA exothermic peaks usually correspond to crystallization temperature (T_c) in glass specimens [20,21]. The results indicate that the crystals form between 895 °C and 1035 °C. Moreover, the broad endothermic hump corresponds to the glass transition temperature (T_g). It can be seen that T_g increases gradually from 580 °C to 650 °C with an increasing amount of CTZ. The increase of T_g could be explained by the fact that Ti⁴⁺, Zr⁴⁺ and Ca²⁺ generates stronger bondings with oxygen atoms than Ba²⁺ and Na⁺ cations that have lower field strength [22,23].

3.2. Crystalline phase and microstructure

Fig. 2 shows XRD patterns of the samples containing different

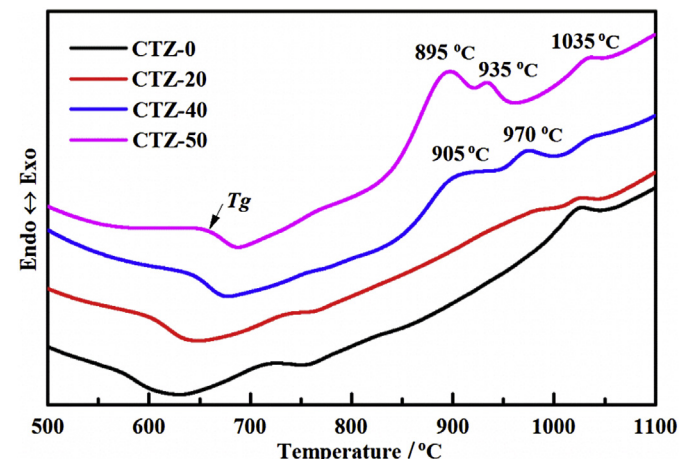


Fig. 1. DTA curves for glasses containing different amount of nucleation agents.

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