



The effects of sulfate content on crystalline phase, microstructure, and chemical durability of zirconolite–barium borosilicate glass-ceramics



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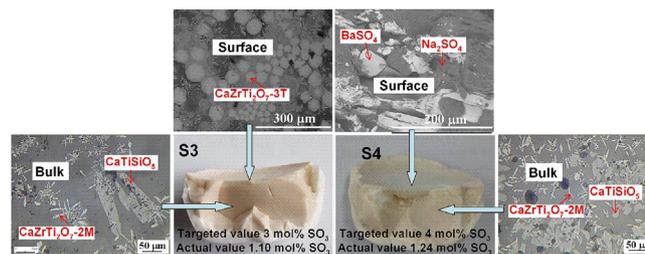
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HIGHLIGHTS

- Strip-shaped $\text{CaZrTi}_2\text{O}_7\text{-2M}$ and plate-like CaTiSiO_5 crystals crystallize in the bulk.
- $\text{CaZrTi}_2\text{O}_7\text{-3T}$ crystals crystallize on the surface for samples with 0–1.10 mol% SO_3 .
- A separate sulfate layer crystallizes on the surface when SO_3 exceeds solubility.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 December 2015

Received in revised form

15 June 2016

Accepted 19 June 2016

Available online 21 June 2016

Keywords:

Barium borosilicate

Glass-ceramics

Zirconolite

Sulfate

Microstructure

ABSTRACT

The effects of sulfate content on structure and chemical durability of barium borosilicate glass-ceramics were studied. The results show that the glass-ceramics with 0–1.10 mol% SO_3 possess mainly $\text{CaZrTi}_2\text{O}_7\text{-2M}$ phase along with a small amount of $\text{CaZrTi}_2\text{O}_7\text{-3T}$ and ZrO_2 phases. The hexagonal $\text{CaZrTi}_2\text{O}_7\text{-3T}$ crystals crystallize on the surface of glass-ceramics. For the samples with 1.24–1.55 mol% SO_3 , the main crystalline phases are CaTiSiO_5 and $\text{CaZrTi}_2\text{O}_7\text{-2M}$ in the bulk, while a separate sulfate layer containing Na_2SO_4 and BaSO_4 is observed on the surface. X-ray fluorescence analysis indicates that about $2/3$ of the SO_3 originally added has been lost by volatility. The normalized mass loss (NL_i) for Na, B, Ca elements remains almost unchanged ($\sim 10^{-2} \text{ g/m}^2$) after 7 days for the samples with 0–1.10 mol% SO_3 . The NL_i for both Na and B increases gradually after 7 days when the SO_3 content is 1.24 mol%.

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1. Introduction

Borosilicate glass has been well accepted by general public to immobilize high level liquid wastes (HLLW) due to its good ability to incorporate many different kinds of waste elements couple with good glass-forming ability, chemical durability, etc. However, the

immobilization of sulfate containing HLLW within commonly used borosilicate glass is difficult due to the limited solubility of SO_4^{2-} ($< 0.6 \text{ mol}\% \text{ SO}_3$) within such melts [1]. Indeed, a separate sulfate layer (popularly known as “yellow phase”) is usually formed on the surface of the borosilicate melts during the vitrification process in some countries [2,3]. Water soluble thenardite (Na_2SO_4) is the most prominent constituent in the yellow phase and acts as a sink for ^{137}Cs and ^{90}Sr , leading to poor chemical durability of waste forms. Moreover, it should also be noted that the solubility of actinides (Np, Pu and Am) in the borosilicate glass is also relatively low

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(~2 wt %) [4], which may act as “waste loading” limiting factor for the immobilization of HLLW. Therefore, it is urgent to develop new matrices for the immobilization HLLW.

In order to prevent formation of the yellow phase in the borosilicate glass, charcoal or sucrose was usually added in the vitreous melts to reduce sulfate to sulfite or sulfur dioxide [5]. However, such addition would cause the vigorous nitrate reduction in the HLLW and another tail gas treatment. Recently, a potential glass matrix based on barium borosilicate has been developed by Kaushik et al. [6] for immobilization of sulfate bearing HLLW. This kind of glass can host up to 21 wt % waste oxide without any phase separation. Later, Mishra et al. [7] investigated the influence of SO_4^{2-} on the three-dimensional barium borosilicate network. The barium borosilicate glass without phase separation was observed when the addition amount of SO_3 reaches up to 3 mol%. Beyond this limit BaSO_4 (barite) crystallized within the barium borosilicate glass matrix. On the other hand, it should be noted that the metastable nature of glass might induce the formation of uncontrolled crystalline phases during the long-term storage in deep geological repositories.

Glass-ceramics containing highly durable crystalline phases have been developed as a very interesting alternative matrix for HLLW immobilization, because such materials possess higher chemical durability, thermal stability, and superior mechanical properties than glass [2,8–14]. Zirconolite ($\text{CaZrTi}_2\text{O}_7$) based glass-ceramic has 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 [11–15]. In recent years, extensive studies have been carried out on $\text{CaZrTi}_2\text{O}_7$ based glass-ceramics belonging to calcium aluminosilicate (SiO_2 – Al_2O_3 – CaO – TiO_2 – ZrO_2) system [12–15].

Our previous work [16] showed that zirconolite-2M and titanite crystalline phases could be obtained when barium borosilicate glass doped with 45–50 wt % CaCO_3 , ZrSiO_4 and TiO_2 (in the mole ratio of 2:2:1). The crystallization mechanism of the barium borosilicate glass-ceramics was also discussed [17]. Nevertheless, SO_3 was not present in the glass-ceramic compositions. The aim of this work is to evaluate the possibility of the zirconolite–barium borosilicate glass-ceramics for the immobilization of sulfur. It is expected that BaSO_4 phase crystallizes within the glass-ceramics instead of Na_2SO_4 phase when the SO_3 content exceeds the solubility limit in the glass matrix. The effects of the SO_3 addition (0–5 mol%, abbreviated as S0, S1, S2, S3, S4, and S5, respectively) on crystalline phases, microstructure, and chemical durability of the barium borosilicate glass-ceramics containing zirconolite phase were mainly investigated in this study. The presence of SO_3 in the glass-ceramics was also analyzed by X-ray fluorescence (XRF).

2. Experimental procedures

The barium borosilicate glass-ceramics were prepared by melting-heat treatment method using the reagent grade of SiO_2 , H_3BO_3 , BaCO_3 , Na_2CO_3 , Na_2SO_4 , CaCO_3 , TiO_2 , Nd_2O_3 , and ZrSiO_4 . The detailed compositions are given in Table 1. The raw materials with

Table 1
Composition of barium borosilicate glass-ceramics (mol%).

Samples	SiO_2	B_2O_3	Na_2O	BaO	CaO	TiO_2	ZrO_2	SO_3
S0	34.08	8.80	6.82	7.10	17.28	17.28	8.64	0.00
S1	33.74	8.72	6.75	7.03	17.11	17.11	8.55	1.00
S2	33.40	8.63	6.68	6.96	16.93	16.93	8.47	2.00
S3	33.06	8.54	6.61	6.89	16.76	16.76	8.38	3.00
S4	32.72	8.45	6.54	6.82	16.59	16.59	8.29	4.00
S5	32.38	8.36	6.48	6.75	16.41	16.41	8.21	5.00

desired compositions at the laboratory scale (~90 g) were mixed thoroughly in an agate mortar and calcined in an alumina crucible at 850 °C for 2 h to decompose carbonates, and then melted at 1250 °C for 3 h in the alumina crucible to form homogeneous melts using muffle furnace. The melts were firstly annealed at nucleation temperatures for 2 h, which are slightly higher than glass transformation temperature T_g , and then annealed at crystal growth temperatures for 2 h.

Glasses were obtained by quenching the melts in cold water, and the quenched glass was crushed and sieved to pass a 100–200 mesh sieve. The glass transformation temperatures and crystal growth 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. 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 ($\lambda = 1.5418 \text{ \AA}$). The bulk samples were firstly etched in 10 wt% HF solution for 10–15 s, and then rinsed with distilled water and sonicated to remove debris. The microstructure was observed using a scanning electron microscope (SEM, S400) fitted with an energy-dispersive X-ray analyzer (EDX) accessory. All the samples were coated with Au for SEM observations. Additionally, some polished bulk samples which were not etched in the HF solution to observe the microstructure using an optical microscope (4XC-PC). The amount of SO_3 in the bulk of glass-ceramics was measured using X-ray fluorescence (XRF, Axios). The chemical durability of the glass-ceramic samples was evaluated with the Product Consistency Test (PCT) at $90 \pm 1.0 \text{ }^\circ\text{C}$ in deionized water (pH = 7) within polytetrafluoroethylene reactors. The leaching powders were crushed and selected by sieving between 100 and 200 meshes. Leachates were taken at regular intervals (1, 3, 7, 14, 28, 42 days). The fines were washed with absolute ethanol and then dried in an oven. Then new deionized water was added in the polytetrafluoroethylene reactors. After the leachates were centrifugated 10 min at a speed of 2000 $\text{r}\cdot\text{min}^{-1}$ using a centrifuge and then acidified with 1 N HNO_3 , they were analyzed by an inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500). The normalized mass loss for element i (NL_i) ($\text{g}\cdot\text{m}^{-2}$) was calculated using the formula given below [18]:

$$NL_i = \frac{C_i \cdot V}{f_i \cdot S}$$

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 samples (m^2), the value of S/V is about 2000 m^{-1} .

3. Results and discussion

Fig. 1 shows the DTA traces of the glass samples S0, S2, S3, and S4 in the temperature range of 400–1200 °C. It can be observed in Fig. 1 that all the DTA curves are similar in nature. The addition of sulfate has no significant change on glass transformation temperatures ($T_g = 630$ – $660 \text{ }^\circ\text{C}$). The T_g decreases slightly with increasing sulfate content. Furthermore, all the samples have a broad exothermic peak at about 850 °C, corresponding to the occurrence of crystallization in the glass. Thus, the heat treatment temperature of glass-ceramics in this work is around 850 °C. The holding time is fixed to 2 h according to our previous works [16,17].

Fig. 2(a)–(d) present the appearance of glass-ceramics S0, S2, S3, and S4, respectively. It can be observed from Fig. 2(a) that S0 (i.e., 0 mol% of SO_3 addition) is opaque and it possesses a dense and uniform structure. Both S2 and S3 show a similar appearance to S0,

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