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Preparation and characterization of SO_3-doped barium borosilicate glass-ceramics containing zirconolite and barite phases

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ABSTRACT

In order to improve the solubility of actinides and sulfate in the glass matrix, barium borosilicate glass-ceramics containing zirconolite and barite crystalline phases were developed. The effects of SO_3 addition (0–8 wt%) on crystalline phases, microstructure, and chemical durability of glass-ceramics belonging to SiO_2-B_2O_3-Na_2O-BaO-CaO-TiO_2-ZrO_2-Nd_2O_3-SO_3 system were mainly studied. The results show that glass transformation temperature decreases slightly with increasing SO_3 content. The main crystalline phase is zirconolite for all of the samples. When the addition SO_3 content is higher or equal to 4 wt%, rice-shaped barite crystals appear in the bulk of glass-ceramics. Barite phase was formed during the melting stage. X-ray fluorescence analysis indicates that about 1.3 wt% of SO_3 can be incorporated in the glass-ceramics when the addition content of SO_3 is 6 wt%. S element mainly distributes in the barite crystals. The decomposition of sulfate mainly occurs during the melting process. Moreover, the addition of a certain content (≤6 wt%) of sulfate has no significant influence on the chemical durability of barium borosilicate glass-ceramics.

1. Introduction

Currently, nuclear scientists are facing the challenges to the management of high-level radioactive wastes (HLW) generated from reprocessing of spent fuel. Borosilicate glass has been widely used for the immobilization of HLW due to its good glass-forming ability, chemical durability, radiation stability, etc [1,2]. However, the immobilization of sulfate bearing HLW in borosilicate glass is very difficult because of the poor solubility of sulfate (< 1 wt% SO_3) in such matrix [3–5]. Beyond the limit, an immiscible phase (popularly known as “yellow phase”) is usually formed on the surface of the melts. Water soluble thenardite (Na_2SO_4) is the main constituent in the yellow phase gathering radioactive elements (^{137}Cs and ^{90}Sr), which leads to poor chemical durability of waste forms [6]. Therefore, it is urgent to develop new matrices for the immobilization of sulfate rich HLW.

It is noted that BaO-B_2O_3-SiO_2 ternary system shows the minimum immiscibility region for the phase diagrams of alkaline earth borosilicate systems [7,8]. Kaushik et al. [9] reported that the addition of BaO in borosilicate glass can significantly improve the solubility of sulfate in the glass matrix. The barium borosilicate glass without any phase separation was observed when the addition amount of SO_4^{2-} reached up to 3 mol% [10]. Hence the barium borosilicate glass is a potential matrix for immobilization of sulfate bearing HLW.

Nevertheless, it should be noted that the glass is a metastable phase in nature, which could form some uncontrollable crystalline phases during the long-term storage in deep geological repositories. On the other hand, the solubility of actinides (Np, Pu and Am) in the borosilicate glass is also relatively low (~2 wt%) [11], which may act as “waste loading” limiting factor for the immobilization of HLW.

Glass-ceramics generally possess the higher durability, thermal stability, and superior mechanical properties as compared with glasses. In addition, highly durable crystalline particles homogeneously dispersed in the bulk of glass matrix will form a double containment barrier for radionuclides [12]. Zirconolite ($CaZrTi_2O_7$), one of the most durable mineral phases on the earth, has an excellent capacity to incorporate actinides into Ca and Zr sites of its structure [13,14]. Therefore, $CaZrTi_2O_7$ based glass-ceramic is of considerable interests, and it has already been studied extensively in recent years. Moreover, among the alkaline earth sulfates, barite ($BaSO_4$) has the highest order of chemical durability and thermally stability. $BaSO_4$ can not only immobilize sulfate, but also incorporate radionuclides such as ^{90}Sr to a large extent [7,10]. If the glass-ceramics contain both zirconolite and barite phases, the loading capacity of actinides and sulfate would be improved significantly.

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

Samples	SiO_2	B_2O_3	Na_2O	BaO	CaO	TiO_2	ZrO_2	Nd_2O_3	SO_3
S0	28.19	11.19	5.54	10.91	11.40	16.24	12.53	4	0
S2	27.61	10.96	5.42	10.68	11.16	15.90	12.27	4	2
S4	27.02	10.73	5.31	10.45	10.93	15.56	12.00	4	4
S6	26.43	10.49	5.19	10.23	10.69	15.22	11.74	4	6
S8	25.84	10.26	5.08	10.00	10.45	14.89	11.48	4	8

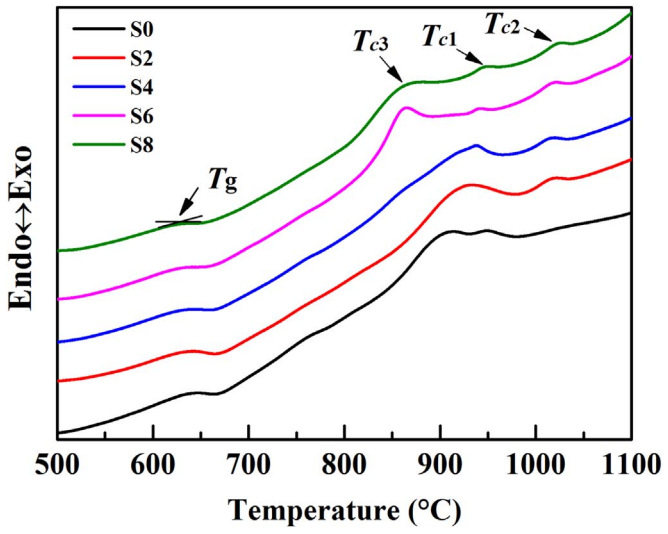

Fig. 1. DTA curves of glass with different SO_3 contents.

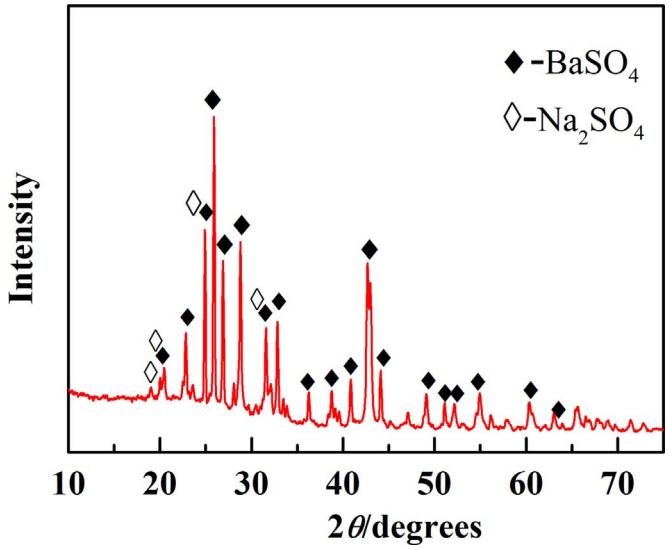

Fig. 3. XRD patterns of the glass-ceramic sample S8.

Our previous work showed that only the zirconolite-2M phase could be found when the total amount of CaO, TiO_2, and $ZrSiO_4$ was 40 wt% in the barium borosilicate glass-ceramics [15]. The effects of sulfate content on structure and chemical durability of zirconolite-barium borosilicate glass-ceramics were also studied. X-ray fluorescence analysis indicated that about 2/3 of the SO_3 originally added were lost by volatility. A separate sulfate layer containing both Na_2SO_4 and $BaSO_4$ was observed on the surface when the addition amount of SO_4^{2-} reached up to 3 mol%. Additionally, the $BaSO_4$ was not present in the bulk of the glass-ceramics [16].

Based on the above consideration, the effects of the SO_3 addition (0–8 wt%, abbreviated as S0, S2, S4, S6, and S8, respectively) on

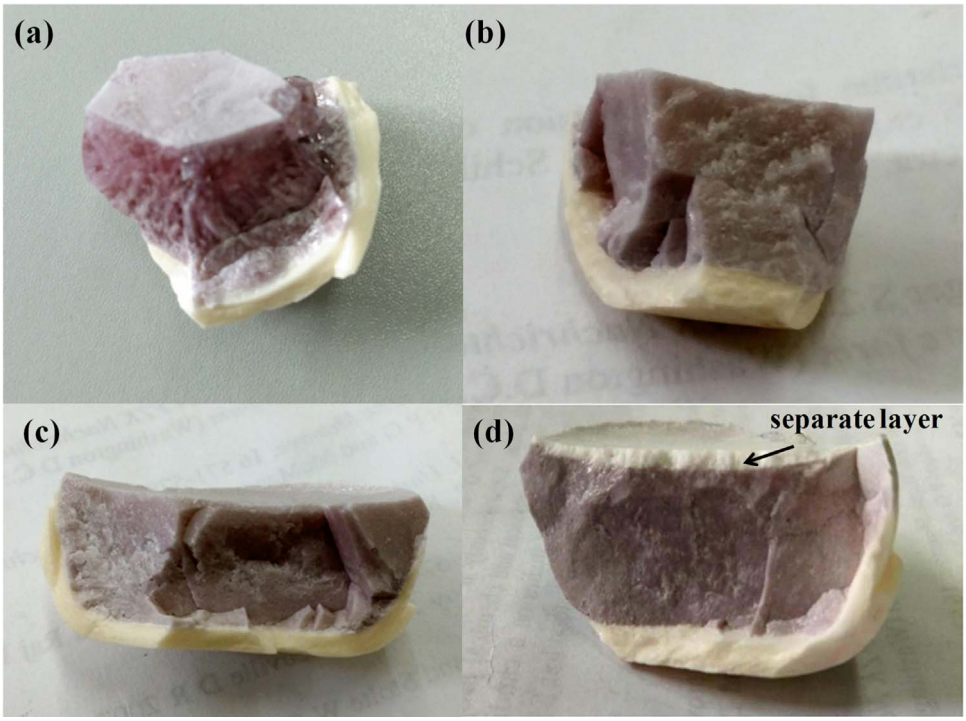

Fig. 2. Appearance of glass-ceramics: (a) S0; (b) S4; (c) S6; (d) S8.