Short communication

A novel Bi-doped borosilicate glass as sealant for sodium sulfur battery. Part 1: Thermophysical characteristics and structure

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ABSTRACT

A novel Bi-doped borosilicate glass has been developed as sealant for sodium sulfur battery. The thermophysical characteristics like thermal expansion coefficient, glass transition and softening temperatures, viscosities and densities of the Bi-doped and undoped glasses are systematically studied. It is found that the thermal expansion match between the Bi-doped glasses and alpha-alumina/beta-alumina is satisfactory. The Bi-doped glass has a viscosity around 10^5 Pa s in 800–850 °C range, which is suitable to allow a good bonding with the sealed parts. The FTIR analysis indicates that the substitution of Bi_2O_3 for SiO_2 makes the glass network less rigid. Bi_2O_3 builds the glass network as $[BiO_6]$ unit. $[BO_4]$ unit enters the glass network and induces the overlapped vibrations of $[BO_4]$ unit and $[SiO_4]$ tetrahedron. The Bi-doped glass sealant exhibits superior chemical compatibility with alpha-alumina and beta-alumina.

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1. Introduction

Sodium sulfur battery which uses sodium and sulfur as electrode active materials and beta-alumina ceramic as the electrolyte is one of the most promising candidates for energy storage technology developed since 1980s [1]. The battery exhibits high power and energy densities, temperature stability, moreover low cost because of its abundant low cost raw materials and suitability for high volume mass production [2].

Sodium sulfur battery operates at a temperature of about 300 °C to keep the electrode materials in a molten state. Hostile reactions would happen between liquid sodium and sulfur in compartments of either side of the beta-alumina electrolyte. For both safety and performance reasons, the seal between the electrolyte, usually beta-alumina, and the insulator, alpha-alumina must be gastight. In addition to achieving a favorable sealing, further requirements such as thermal expansion match, good wetting behavior, thermal shock resistance, chemical stability, corrosion resistance and electrical insulation must be made on the sealant.

Borosilicate glass is well-known for its variety of technological applications. It was early selected as sealant for sodium sulfur battery due to its high mechanical strength and chemical durability [3]. However, the borosilicate glass sealant has inherent disadvantages like high melting temperature, high sealing temperature,

cristobalite precipitation, poor densification and thermal expansion match. The seal creates a major challenge in the development of sodium sulfur battery.

In this work, we developed a novel sealant with improved performances for sodium sulfur battery by doping Bi_2O_3 to the borosilicate glass. The thermophysical characteristics of the Bi-doped and undoped glasses such as thermal expansion coefficient (TEC), glass transition temperature (T_g) and softening temperature (T_s), viscosity and density were investigated, and its structure and chemical compatibility were also studied.

2. Experimental

The composition of the investigated glasses were listed in Table 1. The appropriate amounts of analytical grade SiO_2, Al_2O_3, H_3BO_3, Na_2CO_3, K_2CO_3, Li_2CO_3, and Bi_2O_3 were mixed and heated to melt in Pt crucibles at 1500 °C for 2 h in an electric furnace. The homogeneous melts were poured into a pre-heated stainless steel mold, and annealed at near T_g for 2 h to obtain the bulk glasses. The viscosity of glass GA1 melt was so high that it was unable to be poured off. Therefore, the glass GA1 was not further studied.

The TEC of the glass was measured with a dilatometer (NETZSCH DIL 402C, Germany) from room temperature to 600 °C at a heating rate of 5 °C min⁻¹. T_g and T_s were obtained from the thermal expansion curve. The viscosity range of glass is wide, which needs different methods to determine it in different regions. In this work, the relationship between viscosity and temperature was obtained according to the Vogel–Fulcher–Tamman (VFT) equation

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Table 1
Composition of the Bi-doped borosilicate glasses.

Glass name	Composition (wt.%)						
	SiO$_2$	Al$_2$O$_3$	B$_2$O$_3$	Na$_2$O	K$_2$O	Li$_2$O	Bi$_2$O$_3$
GA0	72	3	18	3	3	1	0
GA1	60	3	18	3	3	1	12
GA2	50	3	18	3	3	1	22
GA3	40	3	18	3	3	1	32
GA4	30	3	18	3	3	1	42
GA5	20	3	18	3	3	1	52
GA6	10	3	18	3	3	1	62

[4]. The method is one of the most convenient and significant methods for viscosity determination. The density was measured by the Archimeds method. The theoretical density of the borosilicate glass was calculated according to Huggins method [5,6]. Fourier transform infrared (FTIR, BRUKER TENSOR 27, Germany) spectroscopy was used to obtain the information of the structure evolution of the glasses as a function of the dopant.
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A beta-alumina sheet (Shanghai Institute of Ceramics, Chinese Academy of Sciences) and alpha-alumina sheet (96% of Al$_2$O$_3$, CeramTec, Germany) about 1 mm thickness, respectively, were used as the materials to be sealed. The glass sealant was placed between beta-alumina and alpha-alumina sheet and heated to 850 °C at 3 °C min^{-1} and held for 7 min. The joints were put into the furnace with 350 °C and held for 200 h to study the chemical compatibility between glass sealants and beta-alumina/alpha-alumina. After the heat treatment, the cross-sections of the joints were polished and the beta-alumina/glass/alpha-alumina interfaces were examined using electron probe micro analyzer (EPMA, 8705QH$_2$, Japan).
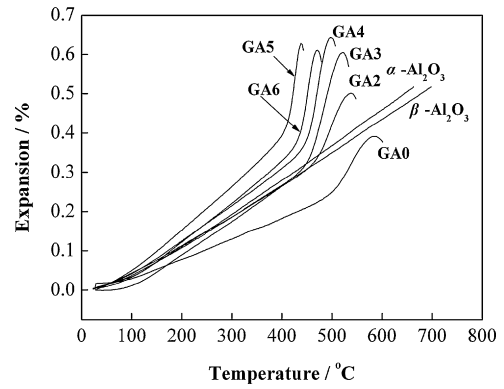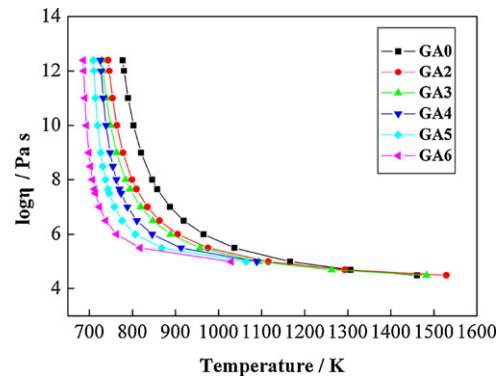
3. Results and discussion

3.1. Thermal behaviors

The thermal expansion curves of Bi-doped and undoped glasses were shown in Fig. 1. The TEC, T_g and T_s of the glasses obtained from the expansion curves were listed in Table 2. As seen, the TEC of the undoped glass was 4.6×10^{-6} °C^{-1} (25–300 °C), which was much lower than that of beta-alumina and alpha-alumina ($6-7 \times 10^{-6}$ °C^{-1}). The substitution of Bi$_2$O$_3$ for SiO$_2$ resulted in an increase in the TEC and induced good thermal expansion match between the glasses GA2–GA4 and alpha-alumina/beta-alumina.

The TEC of glass is not only a function of temperature but also its composition. Furthermore, it is also sensitive to the structure of the glass, e.g., whether the cations occupy the forming or modifying positions in the glass network [7]. The nature of the particular cations should be also taken into consideration. The bond strength and characteristics were suggested to govern the TEC. The loose network favors the increase in TEC. Therefore, the substitution of a cation for another one with higher bond strength will be favorable in increasing the TEC. The addition of Bi$_2$O$_3$ to replace SiO$_2$ obviously increased the TEC and decreased both T_g and T_s of the glasses,

Fig. 1. Thermal expansion curves of the Bi-doped and undoped glasses.

Fig. 2. Viscosity–temperature curves of the Bi-doped and undoped glasses.

which was probably a result of both the lower bond strength of the ions and the looser glass network. The bond strength of Bi–O is lower than that of Si–O, and the glass network became loose with the substitution of Bi$_2$O$_3$ for SiO$_2$, which will also be observed in the following FTIR analysis.

3.2. Viscosity

The viscosity of the investigated glass was calculated according to the Vogel–Fulcher–Tamman (VFT) equation:

$$\log \eta = A + \frac{B}{T - T_o} \tag{1}$$

where A, B and T_o are all constants. Taking glass GA2 as an example, the viscosity was calculated according to Eq. (1). T_g and T_s were 470.7 °C (743.7 K) and 536.5 °C (809.5 K), respectively. There is a relationship between T_g and liquid temperature (T_l) as the following equation expressed [8]:

$$\frac{T_g}{T_l} = \frac{2}{3} \tag{2}$$

Table 2
Thermal expansion coefficient, glass transition (T_g) and softening (T_s) temperatures and densities of the Bi-doped borosilicate glasses.

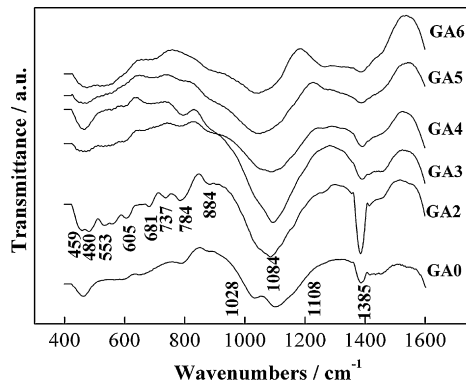| Glass name	Thermal expansion coefficient ($\times 10^{-6}$ °C^{-1})		T_g (°C)	T_s (°C)	d (g cm^{-3})	d_{ct} (g cm^{-3})
	25–300	25–400				
GA0	4.6	4.8	504.3	585	2.20	2.27
GA2	6.6	6.9	470.7	536.5	2.67	2.67
GA3	6.2	6.9	456.0	521.3	2.96	2.91
GA4	7.6	8.1	452.9	497.0	3.38	3.19
GA5	7.7	8.6	436.5	470.5	3.90	3.52
GA6	9.4	10.4	413.1	438.8	4.63	3.94

Fig. 3. FTIR spectra of the Bi-doped and undoped glasses.

T_l was 1115.6 K calculated by Eq. (2). T_l was normally a representative of melting temperature (T_m). Therefore, T_m = 1115.6 K. The characteristic temperatures involving T_g, T_s and T_m are defined as the temperatures corresponding to a specific viscosity, the characteristic viscosities corresponding to T_g, T_s and T_m are $10^{12.4}$, 10^7 and 10^5 Pa s, respectively [6,9,10].

$$T_g = 743.7\,K \rightarrow \eta_g = 10^{12.4}\,Pa\,s,$$
$$T_s = 809.5\,K \rightarrow \eta_s = 4.5 \times 10^7\,Pa\,s, \qquad (3)$$
$$T_m = 1115.6\,K \rightarrow \eta_m = 10^5\,Pa\,s.$$

The constants in Eq. (1) can be resolved by the relationship of characteristic temperatures and characteristic viscosities. The relationship between viscosity and temperature is therefore obtained:

$$\log \eta = 3.99 + \frac{426.39}{T - 693} \qquad (4)$$

The viscosity–temperature relationship of the glass GA2 was obtained according to the above method and was plotted in Fig. 2. The curves of the other glasses were obtained similarly, and were also involved in Fig. 2. As seen, the viscosities of Bi-doped glasses were lower than that of undoped glass at the same temperatures, and the viscosities decreased with the substitution of Bi_2O_3 for SiO_2. Since the glass viscosity depends mainly on the glass network, it was assumed that the substitution of Bi_2O_3 for SiO_2 made the glass network looser and decreased the glass viscosity. It was worthwhile to note that the Bi-doped glass had a viscosity around 10^5 Pa s in 800–850 °C range, which was suitable to allow a good bonding with the sealed parts.

3.3. Density

It is known that the density of a glass responds to its compositions sensitively. The density of a glass, in general, is explained in terms of the atomic mass involved in it [11]. Since the atomic mass of Bi is much larger than that of Si, which resulted in the increase in density with the replacement of SiO_2 by Bi_2O_3 as observed in Table 2.

The theoretical density of a glass could be calculated according to the Huggins method:

$$\frac{1}{d_{ct}} = \sum V_m f_m \qquad (5)$$

where d_{ct} is the theoretical density, V_m the calculating constant of the compositions, f_m the mass percent of the compositions, and the atomic ratio of silicon to oxygen N_{Si} is calculated as [5]:

$$N_{Si} = \frac{Si\ atom\ number}{O\ atom\ number} = \frac{P_{Si}}{M_{Si} \sum S_m f_m} \qquad (6)$$

where P_{Si} is the mass percent of SiO_2 in glass, M_{Si} molecular weight of SiO_2, the constant V_m related to N_{Si} were found in [5]. The theoretical densities of the glasses were calculated with Eq. (5) and listed in Table 2. As shown, the relative density of the undoped glass was 97%, the densities of Bi-doped glasses obtained by Archimeds method were higher than their theoretical densities calculated by Huggins method, indicating fewer pores in the Bi-doped glasses due to their relatively lower viscosities. Moreover, the difference
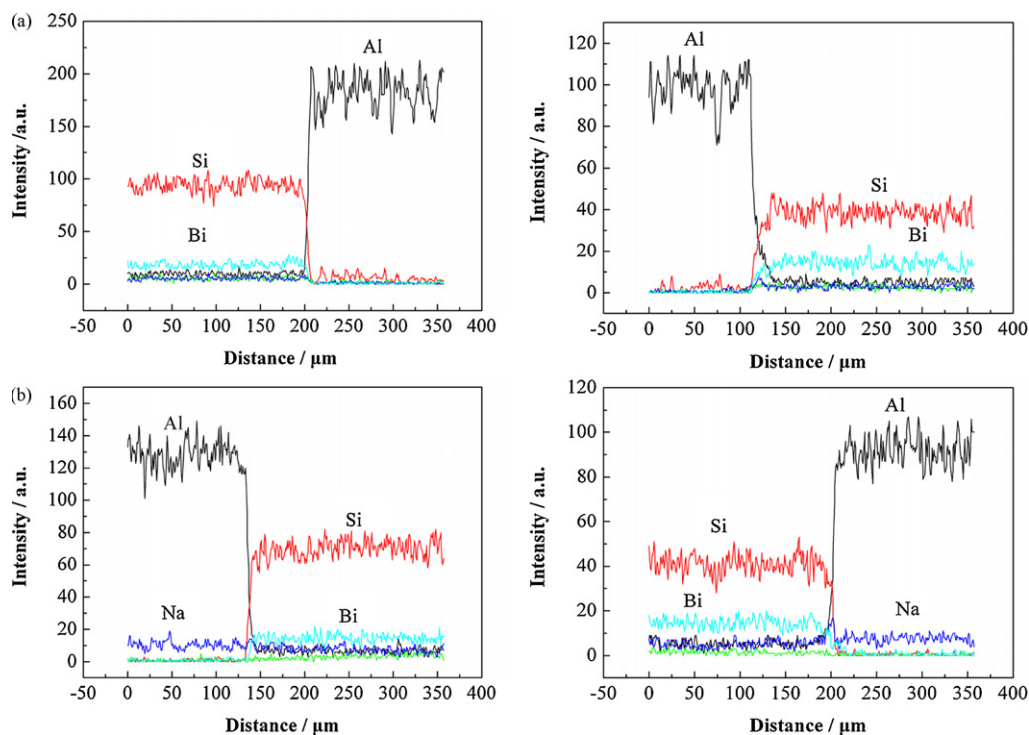

Fig. 4. EPMA line analyses of the interfaces between the glass sealant and alumina heat-treated at 850 °C for 7 min with further treatment at 350 °C for 200 h. (a) Glass GA2/alpha-alumina, (b) glass GA2/beta-alumina, (c) glass GA3/alpha-alumina, and (d) glass GA3/beta-alumina.
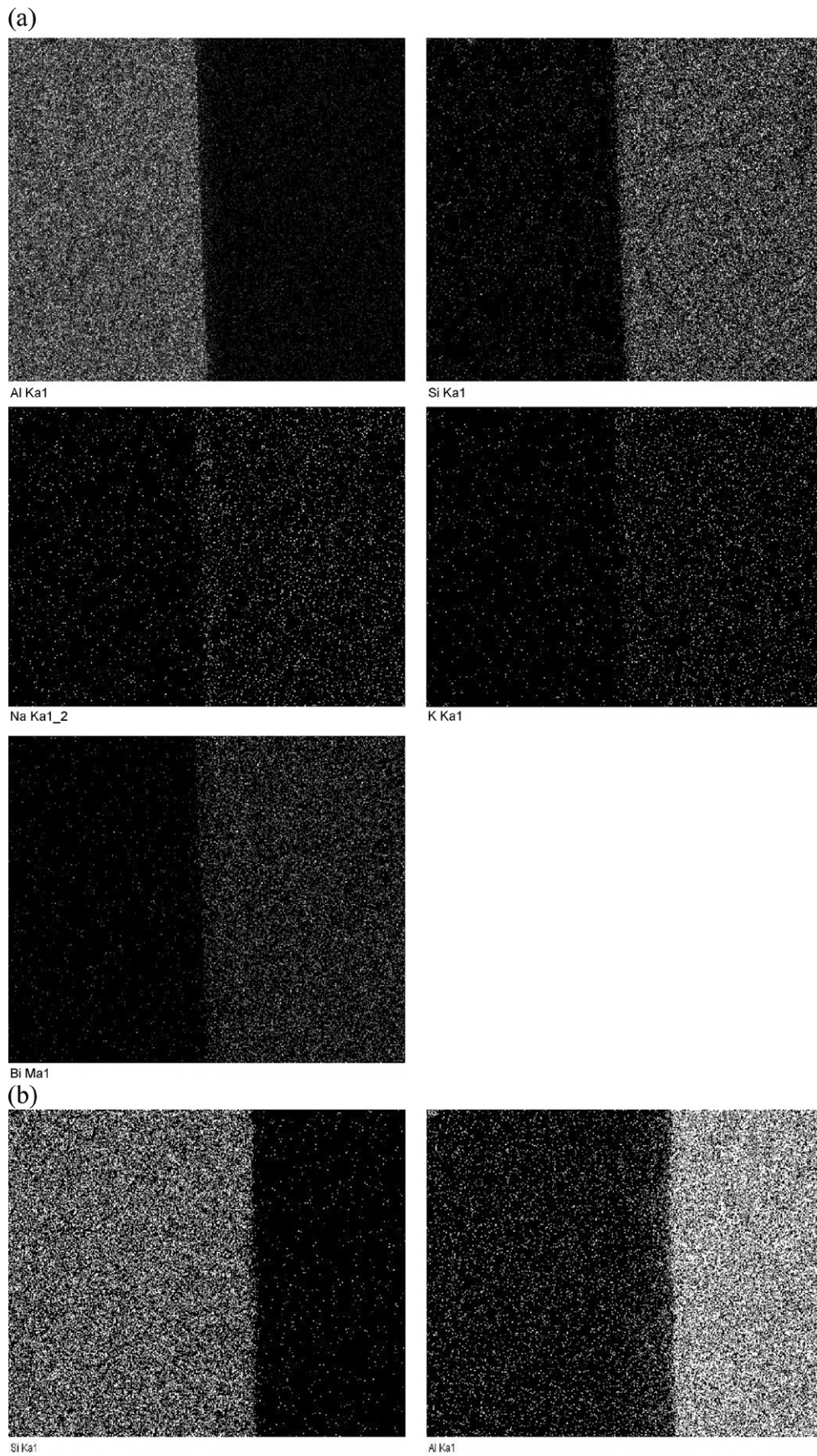
(a)

Al Ka1

Si Ka1

Na Ka1_2

K Ka1

Bi Ma1

(b)

Si Ka1

Al Ka1

Fig. 5. EPMA area mapping analyses for the glass GA3/alumina interfaces heat treatment at 850 °C for 7 min with further treatment at 350 °C for 200 h. (a) GA3/alpha-alumina interface and (b) GA3/beta-alumina interface.

between the tested results and the theoretical values depends on the level of Bi_2O_3 dopant, the higher the Bi_2O_3 contents, the bigger the difference, therefore, the looser structure of the Bi-doped glasses.

3.4. Structure

Fig. 3 shows the FTIR spectra of the as-investigated glasses. The band at about 459 cm^{-1} on the spectra of both series of the glasses could be attributed to the bending vibration of Si–O–Si bond in $[SiO_4]$ tetrahedron, and it was not sensitive to the change of the substitution. The strong broad band located at about 1084 cm^{-1} was attributed to the contributions of the Si–O–Si bond in $[SiO_4]$ tetrahedron. The one at about 784 cm^{-1} was attributed to the vibration of the $[AlO_4]$ tetrahedron. Moreover, the bands at about 1263 and 1397 cm^{-1} were attributed to the stretching vibration of $[BO_3]$ unit [8], and the band at about 681 cm^{-1} was also attributed to the vibration of the $[BO_3]$ unit [12–14]. According to Ref. [15], the band at about 737 cm^{-1} could be considered as the overlapped contributions of $[BO_3]$ and $[BO_4]$ units [15]. The band at about 884 cm^{-1} was related to the vibration of $[BO_4]$ unit [16,17]. The bands at about 480 and 553 cm^{-1} were attributed to the vibrations of $[BiO_6]$ unit [18–20], and the band at about 605 cm^{-1} was attributed to the Bi–O$^-$ stretching vibration in the $[BiO_6]$ unit [21].

As seen in Fig. 3, the main band corresponding to the stretching vibration of Si–O–Si bond in $[SiO_4]$ tetrahedron became broad with the substitution of Bi_2O_3 for SiO_2, indicating that the substitution made the glass network less rigid. For undoped glass, the main band moved to high wavenumber due to the higher SiO_2 content, and the band at about 1028 cm^{-1} could be attributed to the B–O–Si vibration, indicating that $[BO_4]$ unit combined with the vibration of $[SiO_4]$ [22]. As observed in the FTIR result, Bi_2O_3 built the glass network as $[BiO_6]$ unit. As known, Bi_2O_3 is not a classical glass network former, but Bi_2O_3 may build a glass network composed of both $[BiO_6]$ octahedral and $[BiO_3]$ pyramidal units due to high polarizability of Bi^{3+} ions in the presence of conventional glass-forming cations such as Si^{4+}, B^{3+} and Ge^{4+} [19,23]. As seen, the intensity of the band around 1385 cm^{-1} decreased with the substitution of Bi_2O_3 for SiO_2, indicating the decrease of the amount of $[BO_3]$ unit, and the progressive conversion of $[BO_3]$ to $[BO_4]$ unit along with the replacement of SiO_2 by Bi_2O_3. However, the strong vibration of $[BO_4]$ unit in the glasses GA3–GA6 was not detected, probably owing to the overlapped vibrations of $[BO_4]$ unit and $[SiO_4]$ tetrahedron.

3.5. Chemical compatibility

Fig. 4 shows the EPMA curves of the cross-section between the glass sealant and alpha-alumina/beta-alumina heat-treated at 850 °C for 7 min with further treating at 350 °C for 200 h. It was apparent that no diffusion of elements occurred between glass and alpha-alumina but a diffusion layer with the thickness of about 7 μm between glass and beta-alumina would be observed. However, there was an exception between the glass GA3 and alpha-alumina, which could be due to the flaw of the glass/alpha-alumina interface. Fig. 5 exhibits EPMA area mapping analyses for the glass GA3/alumina interfaces heat-treated at 850 °C for 7 min with further treating at 350 °C for 200 h. From the bright points in each image, the distribution of concentration of the elements could be easily observed. As seen in this figure it could be found that no diffusion of Si, Bi, Na and K occurred from glass into alumina. Al did

not diffuse between glass and alpha-alumina, however, it diffused from beta-alumina to glass. EPMA area mapping analyses further favored EPMA line analyses. The 7 μm diffusion layer could be ignored compared with the electrode operation area, which would present little influence on the performance of the electrolyte materials. Moreover, no diffusion of Si, Bi, Na and K occurred from glass into beta-alumina. The glass sealant exhibited superior chemical compatibility with beta-alumina.

4. Conclusions

In this work, a novel Bi-doped borosilicate glass was developed as sealant candidate for sodium sulfur battery. The thermophysical characteristics of the Bi-doped and undoped glasses were systematically studied. The addition of Bi_2O_3 to replace SiO_2 increased the TEC and decreased both T_g and T_s of the glass. The thermal expansion match between the glasses GA2–GA4 and alpha-alumina/beta-alumina was improved by the replacement. The viscosity of the glass decreased with the substitution of Bi_2O_3 for SiO_2. The viscosity was around 10^5 Pa s in 800–850 °C range, suitable to allow a good bonding with the sealed parts. The substitution of Bi_2O_3 for SiO_2 made the glass network less rigid and Bi_2O_3 built the glass network as $[BiO_6]$ unit. The Bi-doped glass sealant exhibited superior chemical compatibility with alpha-alumina and beta-alumina.

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