Multicomponent diffusion in sodium borosilicate glasses

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ABSTRACT

Multicomponent chemical diffusion has been investigated in the SiO_2-Na_2O-B_2O_3 system for melts with an average composition (mol.%) of $68SiO_2$-$18B_2O_3$-$14Na_2O$. Three diffusion couples were studied at 5 different temperatures between 700 °C and 1100 °C. The extended form of Fick's second law was used to fit the data, derive the diffusion matrix at each temperature, and quantify eigenvectors and eigenvalues. The results reveal diffusive mechanisms in chemical space (i.e. eigenvectors) that appear constant over the temperature range studied. The principal eigenvector is characterized by an exchange between silicon and sodium, while the secondary eigenvector corresponds to an exchange between silicon and boron made possible by sodium. Eigenvalues vary considerably with temperature, but do not follow an Arrhenian law. This behavior has been attributed to the structural changes of the borosilicate network with temperature. The diffusion data are then compared with viscosity and ionic conductivity measurements, revealing close links between viscosity and chemical diffusion.

1. Introduction

In France, High Level radioactive Waste (HLW) from spent nuclear fuel reprocessing is incorporated in a multicomponent sodium borosilicate glass. This matrix was selected for its good chemical durability, its low glass synthesis temperature (around 1100 °C) and its ability to incorporate a wide range of radionuclides and fission products [1–3]. The next challenges in the field of nuclear glass research involve finding new glass compositions or optimizing the current formulations, in order to incorporate higher amounts of waste while maintaining chemical durability and attainable synthesis conditions [4]. In this context, a thorough knowledge of the physical and chemical processes that occur in the melt during glass making is essential. In particular, chemical diffusion is of considerable importance given that in the supercooled liquid state, under appropriate thermodynamic conditions, this process can lead to the appearance of crystals that are a source of heterogeneities and may adversely affect long-term stability.

As far as we know, no data on chemical diffusion are currently available for nuclear glasses in the supercooled liquid state. A few studies related to the measurement of self-diffusion coefficients have

been performed, but those experiments were carried out below the glass transition temperature [5–8]. There is therefore a lack of knowledge on chemical diffusion at high temperatures for compositions of interest in the field of nuclear waste management. One reason for this lack of data is that nuclear glasses are multicomponent systems, which makes their study complex. In such systems, Fick's second law in its classical form is insufficient and a more generalized matrix notation must be used to describe diffusion [9–11]. On the other hand, deriving the diffusion matrix is of interest as the eigenvectors and eigenvalues of that matrix contain information that is relevant for describing and understanding diffusive phenomena.

In the literature, the studies on multicomponent chemical diffusion were conducted in metallurgical systems [12–16] and silicate liquids of geological [17–26] and industrial interest [27–35]. Silicate systems were mainly alkaline [18,19,25], alkaline earth [22–24,26,36] or both alkaline and alkaline earth aluminosilicates [17,27]. To the authors' knowledge, only two studies have focused on borosilicates but the diffusion matrices in these systems were not determined [37,38]. In the present contribution, we focus on multicomponent diffusion of simplified borosilicate liquids (in the SiO_2-Na_2O-B_2O_3 ternary) with a target

composition of interest to the nuclear industry.

2. Material and methods

2.1. Choice and synthesis of glasses

2.1.1. Experimental strategy

Diffusion-couple experiments were conducted around a central composition of $67.73SiO_2$–$18.04B_2O_3$-$14.23Na_2O$ corresponding to a simplified version of the French R7T7 waste-disposal glass (the three oxides are kept in the same molar ratio as R7T7 [39]). According to Trial and Spera [40], only two diffusion experiments are necessary to determine the diffusion matrix in a ternary system. However, some authors [17,27,40,41] have shown that adding more experiments is crucial to derive the diffusion matrix more precisely. Therefore, one more couple was added to this work.

The directions of the diffusion couples in concentration space were chosen carefully in order to ensure that no information was missing in the diffusion matrix. Ideally, couple directions should be collinear to eigenvectors in composition space [40]. However, as these vectors are unknown a priori, diffusion directions were chosen in such a way as to be as far as possible from each other. In a ternary representation, this involves having a 60° angle between the three directions (Fig. 1). The difference in composition between the two starting glasses of a given couple was optimized to maintain an acceptable signal to noise ratio during chemical analyses, while keeping chemical variations to a minimum [18] (in case diffusion coefficients vary as a function of composition). With these constraints in mind, glasses were synthesized with a variation of ± 4 mol% in two oxides for each couple. The glasses were labeled *SBNx-y*, where *x* is the SiO_2 molar concentration in the glass and *y* is the B_2O_3 molar concentration (Fig. 1).

2.1.2. Glass synthesis

For each starting glass, a powder mixture corresponding to a decarbonated weight of 100 g was prepared by using reagent grade sodium carbonate, silica and boric acid. The quantities of Na_2CO_3 and H_3BO_3 used were slightly higher than the nominal composition in order to compensate for the effect of boron and sodium volatilization during synthesis. A few ppm of cobalt (CoO powder) were added to one of the

two glasses in each couple in order to color the glass, providing a convenient means of locating the interface after heat treatment. For a given composition, the powder mixture was stirred in a mechanical mixer for 15 min and poured into a $Pt-Rh_{10}$ platinum-rhodium crucible before being placed into a muffle furnace. The temperature was increased from room temperature to 800 °C at a rate of 400 °C/h. It was then kept constant for 30 min to allow Na_2CO_3 decarbonation. After this step, the furnace was heated to 1400 °C at a rate of 400 °C/h. The melt was homogenized for 3 h at this temperature, a time span chosen to ensure bubble-free and crystal-free glass. It was subsequently poured into a preheated carbon crucible with a 2.5 cm² section, and annealed for 1.5 h at 620 °C in another muffle furnace. Finally, samples were cooled to 300 °C at 30 °C/h before the furnace was turned off.
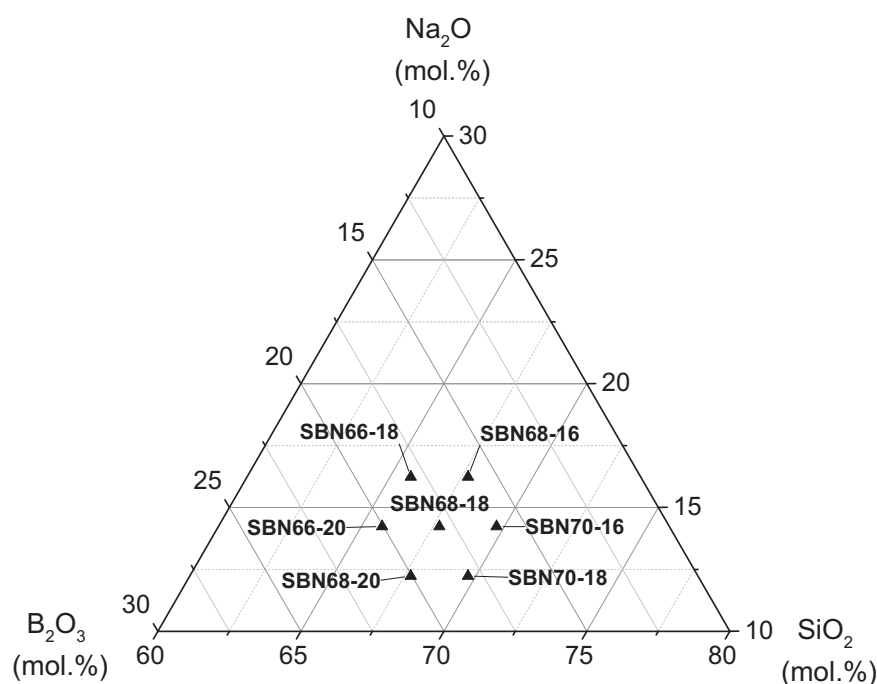
The homogeneity of the glasses was systematically checked by scanning electron microscopy (SEM) and a chip of each glass was also analyzed by electron microprobe, to be sure that its composition was close to that of the nominal composition despite the high volatility of boron and sodium oxides (Table 1).

2.2. Analytical methods

2.2.1. Microprobe

Electron microprobe analyses were conducted for diffusion couples obtained at 900 °C, 1000 °C and 1100 °C. The standard chosen for measuring the SiO_2, Na_2O, and B_2O_3 content was the International Simple Glass (ISG), whose composition is given in Table 2. Two different microprobes were used in this work: a Cameca SX50 (CEA Saclay) and a Cameca SX100 (Lille University). In both cases, the probes were defocused to limit sodium migration under the electron beam, with a 10 μm beam used each time. Operating conditions implemented an accelerating voltage of 15 kV and a beam current of 10 nA. The sodium and silicon contents were measured on a TAP crystal, while a multilayer PC3 crystal was used for boron quantification. Oxygen was calculated by stoichiometry, with counting times of 30, 20 and 10 s for boron, silicon and sodium respectively. Sodium was measured first, in order to improve the accuracy of its measurement. For the analyses performed at Lille University, sodium measurements were made by counting for 2 s, five times in a row. These measurements were regressed to determine the initial sodium content.

Fig. 1. Compositions and names of the glasses used in this study, presented in the ternary SiO_2-Na_2O-B_2O_3 diagram.