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# Solid-state NMR study of bioactive binary borosilicate glasses

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ABSTRACT

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## 1. Introduction

Bioactive glass-ceramic materials have been widely investigated in recent years [1–3]. Glasses that are potential implant materials in the human body must exhibit certain solubility to allow the necessary reactions to take place between the living tissues and the glass surface. In general, the dissolution of a glass involves the processes of leaching and network dissolution. Bioactive glasses prepared by the melt-quench method usually contain < 60% SiO<sub>2</sub> to maintain sufficient solubility. On the other hand, the sol-gel technique has significantly increased the territory of glass compositions exhibiting bioactivity [4-8]. Because tetrahedral or trigonal boron species can enhance the mechanical strength of a glass system, it is of interest to investigate the effect of the boron content on the bioactivity of silicate glasses. Recently, B<sub>2</sub>O<sub>3</sub> has been introduced to bioactive silicate glasses as the second network former in order to tailor the glass dissolution rate [9,10]. The bioactive glasses or glass ceramics containing considerable amount of boron content are basically limited to the system of CaO-Na<sub>2</sub>O-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> prepared by the melt-quench method [9,10]. In this study, we attempt to show that it is possible to prepare B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses with significant bioactivity by the sol-gel method. Tetraethyl orthosilicate (TEOS) and trimethylborate (TMB) in acidic medium are used to prepare  $xB_2O_3 \cdot (1-x)SiO_2$  glasses for x = 0.045 - 0.167. We have characterized the <sup>11</sup>B-<sup>11</sup>B homonuclear second moments of the borosilicate glasses by monitoring the <sup>11</sup>B spin-echo inten-

A series of binary borosilicate glasses prepared by the sol-gel method are shown to be bioactive. Tetraethyl orthosilicate (TEOS) and trimethylborate (TMB) in acidic medium are used to prepare  $xB_2O_3 \cdot (1-x)SiO_2$  glass systems for x = 0.045 - 0.167. The formation of a layer of apatite-like mineral on the glass surface becomes apparent after soaking in simulated body fluid for 48 h. We have measured the <sup>11</sup>B-<sup>11</sup>B homonuclear second moments of the borosilicate glasses and inferred that no macroscopic phase separation occurred in our glasses. The <sup>11</sup>B chemical shift data also show that the formation of clustered boroxol rings is negligible in our glass system. Although the bioactivity of our borosilicate glasses is less than that of CaO-SiO<sub>2</sub> sol-gel glasses, these simple binary systems could be taken as reference glass systems for the search of new bioactive borosilicate glasses.

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sities as a function of the inter-pulse delay. The comparison with the data obtained for vitreous  $B_2O_3$  shows that there is no macroscopic phase separation occurred in our glasses. The <sup>11</sup>B chemical shift data also show that the formation of clustered boroxol rings is negligible in our glass systems. Although the bioactivity of our borosilicate glasses is less than that of CaO–SiO<sub>2</sub> sol–gel glasses, these simple binary systems could be taken as reference glass systems to formulate structure-based principles for the search of new bioactive glasses.

#### 2. Experimental

#### 2.1. Sample preparation

All the chemicals were obtained from Acros and used as received. The desired batches of the glasses were prepared by mixing TEOS and TMB in water–ethanol mixture. Appropriate amount of TMB was added into 50 mL ethanol, which was acidified by HCl (1.5 mL, 12 N) and acetic acid (1.5 mL). After adding TEOS, the mixture was stirred vigorously for 15 min. Water was then added and the mixture was further agitated for another 15 min. The molar ratios of TEOS to water and to ethanol were kept at 1:16 and 1:11.5, respectively. The molar ratio of TEOS to TMB was varied from 1:0.1 to 1:0.5. The sol was hermetically sealed in a polypropylene bottle and placed in an oven for aging. The aged samples were then dried in the oven. The dried gels were stabilized at high temperature to form glasses. The temperature schedules for aging, drying and stabilization are summarized in

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Table 1Temperature schedule for the glass preparation

Stage	Ramp ( °C/min)	Destination temp (°C)	Duration (h)
Aging			
1	0.12	60	5
2	0	60	50
3	-0.12	25	5
Drying			
1	0.12	60	5
2	0.075	150	20
3	0.025	180	20
4	0	180	12
5	-2.6	25	1
Stabilizatio	n		
1	0.88	105	1.5
2	0.25	160	3.7
3	0.5	500	11.3
4	0.046	700	72
5	0	700	1
6	-1.88	25	6

Table 1. Approximately 4 g of borosilicate glass was prepared for each batch. The glasses were then grinded into powder form.

Segments of 200 mg of the glasses were soaked in 500 mL of simulated body fluid (SBF), which was prepared by dissolving MgCl<sub>2</sub>· 6H<sub>2</sub>O (1.50 mM), NaCl (136.9 mM), CaCl<sub>2</sub> (3.76 mM), NaHCO<sub>3</sub> (4.18 mM), K<sub>2</sub>HPO<sub>4</sub>· 3H<sub>2</sub>O (1.00 mM), KCl (3.00 mM) and Na<sub>2</sub>SO<sub>4</sub> (0.50 mM) in deionized water sequentially [11]. Sodium azide (0.01% w/w) was added to suppress bacterial growth. The solution was buffered at 7.4 by tris(hydroxymethyl)aminomethane (53.82 mM) and HCl (43.97 mM). The freshly prepared SBF solution was filtered through a 1 µm filter before use. The glass samples in SBF were incubated in an orbital shaker under 175 rpm at 37 °C for various soaking periods, viz. 48, 64 and 91 h. The glasses were collected by filtration through a 1 µm filter and subsequently rinsed by deionized water, ethanol and acetone. All the samples were dried under reduced pressure for 2 days before measurements.

#### 2.2. Sample characterization

X-ray diffraction (XRD) analysis was performed on a Philips X'Pert diffractometer, using Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The field emission scanning electron microscopy (FE-SEM) and the energy dispersive X-ray (EDX) analysis were done on a JEOL-JSM-6700F field emission scanning electron microscope (operated at 10 kV) equipped with an Oxford INCA energy dispersive X-ray spectrometer. Raman measurements were conducted using a JOBIN YVON HORIBA-HR800 instrument, operating with a Nd/YAG laser at 532 nm. Fourier transform infrared (FT-IR) spectra were collected using a Magna-IR 550 spectrometer (series II), in the range of 400-4000 cm<sup>-1</sup>. All NMR experiments were carried out at <sup>11</sup>B frequencies of 96.3 and 160.4 MHz, respectively, on a Bruker DSX300 and DSX500 NMR spectrometers equipped with a specially designed commercial 4-mm probe (without any significant <sup>11</sup>B background signal). The sample (40 mg) was confined to the middle region of the rotor volume using Teflon spacers. <sup>11</sup>B chemical shifts were externally referenced to BF<sub>3</sub> · Et<sub>2</sub>O, which was sealed in a glass ampoule. Spin-lattice relaxation times  $(T_1)$ were determined by the saturation-recovery technique. Magicangle spinning (MAS) spectra were measured by one-pulse excitation at a spin rate of 10 kHz without proton decoupling. The pulse flip angle was set to 15°, the pre-acquisition delay to  $7\,\mu s$  and the B<sub>1</sub> field to 60 kHz. A total of 120 transients were accumulated for each spectrum and the recycle delay was set to 5 s. The line shape deconvolution was carried out by the package DMfit2003 [12]. <sup>11</sup>B spin-echo measurements were carried out under static condition at 11.74 T (160.4 MHz). The selective  $\pi/2$  pulse was set to 4.2 µs. This condition corresponds to the selective excitation of the central transition, as was ascertained by the observation of strictly sinusoidal nutation profile.

## 3. Results

## 3.1. Glass structure

A series of borosilicate glasses were prepared with different molar percentages of B<sub>2</sub>O<sub>3</sub>, viz. 4.5, 12.5 and 16.7 mol%. All the glass samples will be henceforth labeled based on their percentage contents of B<sub>2</sub>O<sub>3</sub>. XRD measurements show that no crystalline phases are present in our glass samples. Fig. 1 shows the <sup>11</sup>B MAS spectra measured for the glass samples at 7.05 and 11.74 T. which exhibit typical features arising from the second-order quadrupolar broadening [13]. The NMR data summarized in Table 2 were determined by the line shape deconvolution and the spectra at two fields were simulated by the same set of NMR parameters for each sample. The fits are not perfect as commonly observed for glassy materials because each of the NMR parameters has a distribution about a mean value [14]. Clearly, there are no tetrahedral boron sites found and this observation is consistent with the notion that network modifiers such as alkalior alkaline oxide are required to convert BO<sub>3</sub> units to BO<sub>4</sub> units. For each of our samples, there is only one major boron species which can be identified as BO<sub>3/2</sub> because the asymmetry parameters  $\eta_0$  determined are significantly less than 0.5 [14,15]. Recently, it has been reported that the <sup>11</sup>B chemical shifts of the boroxol rings and the non-ring BO<sub>3/2</sub> units in a series of borosilicate glasses are in the range of 15.7-17.4 and 11.0–12.5 ppm, respectively, in which the boron species become more deshielded as the boron content increases from 28 to 100 mol% [16]. Also, the <sup>11</sup>B chemical shift of BO<sub>3/2</sub> unit connected to three silicon atoms was found to be 9.7 ppm [17]. The isotropic <sup>11</sup>B chemical shifts observed for our glasses are in the range of 12.8–13.3 ppm. Consequently, we can rule out the existence of the B-(OSi-)<sub>3</sub> species in our glasses. The formation of a network of inter-connected boroxol rings in our glasses is also unlikely. In an earlier report, however, clustered boroxol rings were found in a borosilicate glass system containing 5 mol% of B<sub>2</sub>O<sub>3</sub>, which was prepared by sol-gel method in alkaline medium [18]. It was estimated that only 66% of the BO<sub>3/2</sub> units mixed statistically with silica tetrahedra and the rest formed a borate network, resulting in the formation of boroxol rings [18]. Apparently, a more homogeneous glass matrix can be obtained in acidic medium as demonstrated in this work.

To probe for the connectivities among the boron units, we measured the  ${}^{11}B{-}{}^{11}B$  van Vleck's second moments of our glass samples by spin-echo decay spectroscopy. A detailed discussion of this approach is well documented in the literature [19–21]. In brief, the normalized echo intensity,  $I(t)/I_0$ , is measured as a function of the evolution time (2 $t_1$ ). For a multi-spin system, a Gaussian decay is expected in the limit of short dipolar evolution times (2 $t_1$  < 200 µs):

$$\frac{I(2t_1)}{I_0} = \exp\left[-\frac{M_2}{2}(2t_1)^2\right]$$

With reference to the results shown in Fig. 2, the  $BO_{3/2}$  units have a strong tendency to form B–O–B linkages. Nevertheless, because the extracted second moments of the glasses are considerably less than that determined for the vitreous  $B_2O_3$ 



Fig. 1. <sup>11</sup>B MAS spectra of the glass samples measured at 7.05 and 11.74T. The solid and dashed traces correspond to the experimental and simulation spectra, respectively.

 Table 2

 NMR parameters extracted by line shape deconvolution of <sup>11</sup>B MAS spectra<sup>a</sup>

Sample	$\delta$ (ppm)	η	$C_{\rm Q} ({\rm MHz})$
B-16.7 B-12.5 B-4.5	$\begin{array}{c} 13.3 \pm 0.1 \\ 12.8 \pm 0.3 \\ 12.8 \pm 0.1 \end{array}$	$\begin{array}{c} 0.14 \!\pm\! 0.01 \\ 0.15 \!\pm\! 0.01 \\ 0.13 \!\pm\! 0.01 \end{array}$	$\begin{array}{c} 2.62 \pm 0.02 \\ 2.61 \pm 0.03 \\ 2.63 \pm 0.03 \end{array}$

<sup>a</sup> The <sup>11</sup>B spin-lattice relaxation time was found to be c.a. 1.7 s.



**Fig. 2.** Dependence of the <sup>11</sup>B-<sup>11</sup>B second moments on the boron content in mol %. The inset shows the raw data of the spin-echo measurements. The solid line is the Gaussian-decay curve fitted to the vitreous  $B_2O_3$  data in the limit of short dipolar evolution times ( $2t_1 < 200 \,\mu$ s).

sample, we conclude that there is no macroscopic phase separation occurred in our glasses. In principle, one may also employ other sophisticated NMR techniques such as double-



Fig. 3. Raman spectra of the glass samples. The small peak at  $600 \, \text{cm}^{-1}$  (marked by an arrow) is attributed to Si–O–B linkages.

resonance methods to investigate the medium-range order of the boron units [22] but such a detailed NMR study is beyond the scope of this work.

Fig. 3 shows the Raman spectra measured for our glasses and the vitreous  $B_2O_3$  sample. The intensity of the band at  $808 \text{ cm}^{-1}$ increases with the percentage of B<sub>2</sub>O<sub>3</sub>. In comparison with the spectrum measured for pure B<sub>2</sub>O<sub>3</sub>, this band can be attributed to the vibrations of the B-O-B linkages [23-25]. The absence of a peak at  $795 \text{ cm}^{-1}$  confirms that there is no BO<sub>4</sub> unit present in our glasses [26]. A small peak at  $600 \text{ cm}^{-1}$  is attributed to Si–O–B linkages [27]. The most intense band centered at 450 cm<sup>-1</sup> is assigned to the vibrations of the Si-O-Si bonds [24,27]. In the literature, the weak bands at around 950 and 1090 cm<sup>-1</sup> were assigned to the stretching Si–O vibration in  $Q^2$  and  $Q^3$  species [27]. However, <sup>29</sup>Si NMR data show that SiO<sub>4/2</sub> units are the major species in our samples and the amount of  $Q^2$  and  $Q^3$  species, if any, are very low (Supporting Information). We note in passing that <sup>17</sup>O NMR has been shown to be an effective method to probe and quantify the nature of bridging oxygen species in borosilicate glasses [28,29].

## 3.2. Bioactivity

To examine whether our borosilicate glasses have bioactivity, we follow the standard practice by soaking the samples in SBF for different periods [2], viz. 48, 64 and 91 h. Fig. 4 shows the SEM images of the B-12.5 sample before and after soaking in SBF for 48 h. The SEM results show that the minerals deposited on the glass surface have morphologies similar to the crystal habits of apatites formed on bioactive glasses. The average Ca/P ratio is determined to be 1.53 by EDX analysis, which is similar to what we expected for apatites formed on bioactive glass surface [30]. Additional SEM images were obtained for samples with longer soaking times and we found that more minerals were deposited as the soaking time increased. To identify the minerals formed on the glass surface, the XRD patterns of our sample series were measured. The results obtained for B-12.5 are shown in Fig. 5. After soaking the sample for 48 h, two broad peaks at  $2\theta$  equal to 26° and 32° becomes apparent, suggesting the incipient formation of a low crystallinity apatite-like phase on the glass surface [31]. As the soaking time increases further to 91 h, the peak intensities become more prominent. However, the resolution of the diffraction pattern remains poor, which could be attributed to the poor crystallinity and/or the nanosize of the crystallites. Similar results were obtained for other glasses with different boron contents (data not shown). As a control experiment, a powder sample of Pyrex glass was soaked in SBF for 91 h and no XRD diffraction peaks were observed.

Fig. 6 shows the FT-IR data measured for the B-12.5 sample with different SBF soaking periods. The absorption peaks observed in the 64 h sample in the regions of 560 and  $600 \text{ cm}^{-1}$  are assigned to the P–O bending mode [32–34], which becomes more intense as the soaking time increased to 91 h. The small peak at 875 cm<sup>-1</sup> is assigned to the CO stretching of  $CO_3^{2-}$  ions [8,35]. This CO stretching peak was also observed in other studies [8,34].



Fig. 5. XRD patterns for the B-12.5 sample soaked in SBF for different periods.



Fig. 4. SEM images of the B-12.5 sample. (a) Without soaking in SBF; (b) after soaking in SBF for 48 h. The scale bars correspond to 10 and 1 µm in (a) and (b), respectively.



Fig. 6. FT-IR spectra of the B-12.5 sample soaked in SBF for different periods.

## 4. Discussion

For the sol-gel preparation of borosilicate glasses, it is important to avoid macroscopic phase separation. The key is to select suitable reaction conditions so that the hydrolysis rates of the silicon and boron precursors are similar. Although TEOS is a common precursor to synthesize silicate materials, there are many different boron precursors reported for the sol-gel preparation of boron-containing glasses [36–41]. Typical examples are boron oxide and boron alkoxides, B(OR)<sub>3</sub>. Some years ago, it had been reported that no B-O-Si bonds would exist in the gels prepared by tetrafunctional silicon alkoxides and trialkylborates because of the high hydrolysis rate of B-O-Si linkages [42,43]. Consequently, modified silicon alkoxide R'-Si(OR)<sub>3</sub> are developed to prepare the  $SiO_2-B_2O_3$  gel, in which the  $BO_3$  units are homogeneously dispersed in the SiO<sub>2</sub> network via B–O–Si bonds [44]. Nevertheless, in this study we demonstrate that a mixture of TMB and TEOS can be used to prepare considerable B-O-Si linkages when the reaction conditions are carefully optimized. Although our NMR instrument does not allow us to perform any <sup>29</sup>Si-<sup>11</sup>B double resonance experiment to directly probe the formation of B–O–Si linkages, the <sup>11</sup>B NMR data and the Raman results provide supporting evidence for their existence.

The bioactivity of our borosilicate glasses is unequivocally demonstrated in the SBF soaking experiments. Additional <sup>31</sup>P MAS NMR experiments (Supporting Information) show that the amount of phosphate material deposited on the surface of our borosilicate glasses is less than that on the CaO (30%)–SiO<sub>2</sub> (70%) gel glass, which requires an SBF soaking time of 12 h only for the formation of an apatite-like phase on the surface [30]. In view of the significantly longer incubation time required for the incipient formation of apatite-like minerals, the bioactivity of our borosilicate glasses is considerably less than those of Na<sub>2</sub>O–SiO<sub>2</sub> and CaO–SiO<sub>2</sub> sol–gel glasses. This observation is consistent with the

notion that the leaching process of alkali or alkaline-earth ions will induce the formation of apatite-like mineral on the glass surface [1,2].

## 5. Conclusion

In this work we have prepared a series of binary borosilicate glasses by the sol-gel method. The <sup>11</sup>B NMR data show that the formation of clustered boroxol rings is negligible in our glass system. The bioactivity of our borosilicate glasses is unequivocally demonstrated in the SBF soaking experiments. The formation of a layer of apatite-like mineral on the glass surface becomes apparent after soaking in SBF for 48 h.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jpcs.2008.06.004.

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