The effect of composition on the viscosity, crystallization and dissolution of simple borate glasses and compositional design of borate based bioactive glasses

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THE EFFECT OF COMPOSITION ON THE VISCOSITY, CRYSTALLIZATION 
AND DISSOLUTION OF SIMPLE BORATE GLASSES AND 
COMPOSITIONAL DESIGN OF BORATE BASED BIOACTIVE GLASSES

by

KATHRYN LYNN GOETSCHIUS

A DISSERTATION

Presented to the Faculty of the Graduate School of the 
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PUBLICATION DISSERTATION OPTION

The Introduction and Background sections of this dissertation provide information about the research topic, and a review of the literature. The body of this dissertation has been compiled in the format for publication in peer-reviewed journals. Four papers have been included. The first paper, pages 17-49, “Viscosity, Crystallization and Glass Forming Tendency of Na$_2$O-CaO-B$_2$O$_3$ Melts” was prepared for submission to Physics and Chemistry of Glasses. The second paper, “Spectroscopic study of the structure of ternary alkali-alkaline earth-borate glasses” pages 50-69, and third paper, “Dissolution behavior of ternary alkali-alkaline earth-borate glasses” pages 70-95, and were prepared for submission to the Journal of Non-Crystalline Solids. The fourth paper, pages 96-121, will be submitted to the special issue "Glasses in healthcare" a compilation of papers from the Health, Medical, Biological Aspects – Fundamentals and Application symposium at the DGG-GOMD conference in Aachen, Germany, to be published in the Journal of Non-Crystalline Solids.
ABSTRACT

Borate glasses have recently been developed for a variety of medical applications, but much less is known about their structures and properties than more common silicate glasses. Melt properties and crystallization tendency for compositions in the Na$_2$O-CaO-B$_2$O$_3$ system were characterized using differential thermal analysis and viscosity measurements. Characteristic viscosity (isokom) temperatures varied with the ratio between the modifier content (Na$_2$O+CaO) and B$_2$O$_3$, particularly at lower temperatures, consistent with the changes in the relative concentrations of tetrahedral borons in the glass structure.

Similar glasses were used to study dissolution processes in water. These alkali-alkaline earth glasses dissolve congruently and follow linear dissolution kinetics. The dissolution rates were dependent on the glass structure, with slower rates associated with greater fractions of four-coordinated boron. For glasses with a fixed alkaline earth identity, the dissolution rates increased in the order Li<Na<K. For glasses with a constant alkali identity, the dissolution rates increased in the order Ca<Sr<Mg. The effects of different alkali and alkaline earth oxides on dissolution rates are discussed in terms of competing effects of four-coordinated boron and the field strength of the modifying cation.

Finally, a seven component (Na$_2$O, K$_2$O, MgO, CaO, B$_2$O$_3$, SiO$_2$, and P$_2$O$_5$) mixture model design was used to predict composition-property relationships to optimize the properties of new borate-based bioactive compositions for specific applications. Melt viscosity, thermal expansion coefficient, liquidus temperature and crystallization tendency were determined, as were dissolution rates in simulated body fluid (SBF).
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1. INTRODUCTION

1.1. BIOACTIVE GLASSES

Silicate glasses have been used for biomedical applications since Hench first developed Bioglass (45S5) [1] in the 1960’s. Another silicate glass composition that is commonly used is 13-93 [2]. Both of these glasses were designed for applications where bioactivity is important such as bone scaffolding, ear implants, toothpaste and coatings for implants [3]. Hench based 45S5 on the Na$_2$O-CaO-SiO$_2$ ternary phase diagram with 6 weight percent P$_2$O$_5$. Initial compositions were near the ternary eutectic and a composition was found that when it reacts in vivo will bond to bone; the Bioglass composition will bond to soft tissue as well. One of the negative issues with 45S5 that led to the development of 13-93 was the former’s tendency to crystallize during sintering. The 13-93 glass was intentionally designed to minimize unwanted crystallization while tailoring other properties, such as viscosity and dissolution rate.

Borate glasses such as DermaFuse, produced by Mo-Sci Corporation, have recently been developed for biomedical applications [4, 5]. In the presence of phosphate-containing solutions, including simulated body fluid, and under in vivo conditions, calcium containing borate glasses convert to hydroxyapatite (HAp) more quickly than do
silicate bio-glasses. Borate glasses are also good hosts for ions that can promote healing [6].

1.2. TAILORING COMPOSITIONS FOR BIOACTIVE GLASSES

In order to design a bio-active glass composition for bioactive applications, several factors need to be considered. Hupa’s group in Finland has developed many bioactive silicate glass compositions and gives an overview of the process [7]. The main aspects for design include the viscosity [8], crystallization characteristics [9] and the in vitro reactivity [10] of the glasses.

1.3. BORATE GLASS STRUCTURE

The structure of borate glasses differs from that of silicate glasses. In silicate glasses the addition of alkali or alkaline earth oxides causes the formation of non-bridging oxygen (NBO). This decreases the connectivity of the structure and the effects of these structural changes can be seen in the decreasing trend in the glass transition temperature ($T_g$) [11].

Alkali or alkaline earth oxide additions (modifiers) do not have the same effect in borate glasses. Initially, the additions of modifiers cause a coordination change from a three-coordinated, trigonal borate
unit (BØ₃) to a four-coordinated, tetrahedral borate unit (BØ₄⁻) [12]. This is because the oxygen associated with the modifying oxide is incorporated into the structure in a boron tetrahedron with the cation acting to charge balance the unit instead of forming a NBO as it does in a silicate glass. This causes an increase in the connectivity of the network structure. After the modifier concentration reaches approximately 30 mole % this trend changes. This concentration marks where the BØ₄⁻ units will no longer be surrounded by BØ₃[13, 14]. Additional modifiers will cause the conversion of the BO₄⁻ to three-coordinated borate units with NBO (BØ₂O⁻ or BØO₂⁻). Empirical models have been used to describe the fraction of BØ₄⁻ units (fBØ₄⁻) in a glass. See Eq. 1, for 0<x<33, and Eq. 2, for x>33, where x is the mole percent of the modifier (ie. xNa₂O-(100-x)B₂O₃) [11].

Eq. 1  \[ fB4 = \frac{x}{100-x} \]

Eq. 2  \[ fB4 = \frac{300-4x}{500-5x} \]

This boron coordination change and the associated property changes are referred to as the borate anomaly. Additions of alkali [15] or alkaline earth oxides are assumed to have similar effects on the structure[16-18] . However, some studies have found that the behavior of alkaline earth containing glasses will diverge from this
simple model based on information from nuclear magnetic resonance (NMR) [18], nuclear diffraction (ND) and molecular dynamic simulation (MD) [17] experiments.

Typical methods for determining the structure of glasses include NMR and Raman spectroscopy [19-21]. NMR is capable of measuring the relative concentrations of BØ₄⁻ and BØ₃ units in the sample [18] whereas Raman spectroscopy will provide information about the intermediate range order [21].

1.4. VISCOSITY, GLASS STABILITY AND GLASS FORMING

In order to expand the possible applications for borate bio-glasses, a borate glass composition capable of continuous fiber drawing is desired. For example, one type of scaffold used for tissue engineering is made of fibers that are sintered by heating in a mold at a temperature between the glass transition temperature (T_g) and the onset of crystallization temperature (T_x) [5]. Fiber diameters can be controlled by the pulling rate and depend on the viscosity of the melt. Unintentional crystallization could make it difficult to continuously pull fibers from a melt, and could lead to the formation of phases that would be more difficult for the body to resorb. In addition, a partially crystallized scaffold may have different mechanical properties that
would in turn affect its application. Current borate glass compositions
tend to crystallize during drawing [unpublished results].

The glass forming ability describes the likelihood of a melt to
avoid crystallization and form a glass on cooling. The glass stability
describes the resistance of a glass to crystallization upon heating
above the glass transition temperature, \(T_g\) [22].

The relative glass stability for a composition can be estimated
from characteristic temperatures determined from differential thermal
analysis (DTA), including the glass transition temperature (\(T_g\)), the
onset of crystallization (\(T_x\)) and the onset of melting (\(T_m\)). There are
different glass stability parameters reported in the literature, including
the Angell [23] (Eq. 3) and the Weinberg [24] (Eq. 4) and the Hruby
[25] (Eq. 5) parameters.

\[
\begin{align*}
\text{Eq. 3} & \quad K_A = (T_x - T_g) \\
\text{Eq. 4} & \quad K_W = (T_x - T_g) / T_m \\
\text{Eq. 5} & \quad K_H = (T_x - T_g) / (T_m - T_x)
\end{align*}
\]

The term \((T_x - T_g)\) indicates a general resistance to crystallization
[26]; a smaller interval means that the glass is likely to crystallize.
The term \((T_m - T_x)\) is an indication of how readily the crystalline phase,
onece formed, will melt. The smaller this term the easier it is for the
melt to be cooled through the range where it is likely to crystallize. Similarly, the lower the melting temperature, $T_m$, for the crystal that is formed the shorter the temperature range need to cool through to avoid crystallization as well. $K_A$ is of interest because this defines the temperature range that is often used for sintering scaffolds from glass fibers and powders [27]. For all parameters, larger values indicate greater glass stability against crystallization.

The glass forming ability of a melt depends on how quickly a composition needs to be cooled from a melt to a solid. Critical cooling rates have been used to determine glass forming ability, however they can be difficult to determine [28, 29]. Attempts have been made to relate glass stability parameters to critical cooling rates; however, systems that show a strong preference for surface nucleation are not well suited for the use of this technique. Instead the temperature-viscosity curves of a melt can be used to provide a method for determining the glass forming ability. Melts that are more viscous at the liquidus temperature are less likely to crystallize on cooling and will thus form a glass more readily [30, 31]. In viscous melts, crystallization is hindered by slower diffusion. In fluid systems, like these borate melts, glass-forming ability has to be determined by another parameter; i.e., how rapidly the viscosity of the melt changes with decreasing temperature. One measure of the change in viscosity
near the glass transition temperature is the fragility parameter [32]. Fragility can be determined either by heat capacity measurements or from viscosity measurements. The MYEGA model [33] for viscosity uses fragility (m), the glass transition temperature, \( T_g \) and the log of the viscosity at infinite temperature \( \log_{10} \eta_\infty \) as the parameters to describe the overall viscosity-temperature curve.

\[
\log_{10} \eta(T) = \log_{10} \eta_\infty + (12 - \log_{10} \eta_\infty) \frac{T_g}{T} \exp\left[\frac{m}{12 - \log_{10} \eta_\infty - 1}\left(\frac{T_g}{T} - 1\right)\right]
\]

Eq. 6

The reduced glass transition temperature \( T_{rg} = T_g / T_{liq} \) has also been used to indicate the glass forming ability of a melt. Greater values of \( T_{rg} \) mean smaller temperature ranges over which supercooled melts must be quenched to avoid crystal formation. There is also a correlation between \( T_{rg} \) and the tendency of a super-cooled liquid towards either surface or bulk nucleation. If \( T_{rg} \) is greater than \( \approx 0.58 \), then the glass will display only surface nucleation within the laboratory time scale [28, 34, 35]. Better glass formers tend to avoid internal nucleation of crystals.

1.5. **BORATE GLASS DISSOLUTION AND CORROSION**

The dissolution processes associated with alkali-containing borate glasses differ from those associated with alkali-containing silicate glasses. The early stages of silicate glass dissolution are
controlled by an ion exchange reaction between the alkalis and protons in solution, to produce a hydrated silica gel surface layer [36]. For borate glasses, hydrolysis of the borate network occurs simultaneously with the leaching of the modifying ions. The constant dissolution rate indicates a reaction controlled mechanism and is considered congruent dissolution [37]. This is likely due to the high solubility of borate anions in water [38] and leads to faster dissolution of borate glasses compared to silicate glasses with similar alkali and alkaline earth contents. Lowry [39] studied the dissolution behavior of $x\text{Na}_2\text{O}-x\text{CaO}-(100-2x)\text{B}_2\text{O}_3$ glasses, where $5 \leq x \leq 20$ mole percent and found that the slowest dissolution rates occurred for glasses with a total modifier content of 30-35 mole percent, in water as well as different buffered solutions, corresponding to the highest fraction of tetrahedral borates, $\text{fBO}_4^{-}$, in the glass structure. These glasses showed congruent dissolution in deionized water, and in solutions buffered at pH=4, 7 or 10.

Typically, glasses that form hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) when reacted in a phosphate containing solution are considered to be bioactive [40]. It is worth noting that this definition of bioactivity is based on the potential of a material to bond to living tissue, including bone [41]. Hydroxyapatite is a main component of bone, however in the body it is not likely to be stoichiometric. Most hydroxyapatite found
in the body is carbonated or calcium deficient [42]. When the glass dissolves, it releases calcium ions that will react with the phosphate ions in solution to form an amorphous calcium phosphate layer. This calcium phosphate layer will eventually crystallize into hydroxyapatite [43].

The reaction of simple ternary borate compositions in phosphate-containing solutions has been studied [43-45] as well as borate/borosilicate analogues of 45S5 [46, 47] and 13-93 [48]. The reaction of the borate based glasses can be initially described by a reaction-controlled contracting volume model and then by a diffusion controlled model at longer times [49]. This switch in mechanisms is likely due to the formation of a hydroxyapatite surface layer on reacting glass particles which affects subsequent reaction rates.
2. PURPOSE OF THIS DISSERTATION

The goal of this work was to determine the effects of different components on the viscosity, crystallization and dissolution behavior of borate glasses. This information can then be used to design a borate glass composition for use in the human body by optimizing the viscosity, crystallization characteristics, and corrosion behavior.

The first stage of this work was to determine the viscosity and crystallization characteristics of glasses and melts in the Na$_2$O-CaO-B$_2$O$_3$ system, especially the higher CaO-content compositions of interest for biomedical applications. This information provided a basis to both avoid unwanted crystallization as well as to tailor the viscosity of the final composition.

The second stage of this work was to determine how different alkali and alkaline earth ions affect the dissolution behavior of borate glasses in aqueous environments. This information can be used to tailor the glass reactivity for desired applications. The effect of the composition on the glass structure and thus the dissolution rate have been determined.

The third stage of this work was to complete a seven-component design of experiments study to identify new bioactive borate glass compositions with properties optimized for biomedical applications. These properties include: a melt viscosity that allows for continuous
fiber drawing, glass stability during sintering to form a scaffold, and controlled conversion to hydroxyapatite. These properties were studied using glass forming ability parameters previously used in the first section and the glass dissolution in simulated body fluid in conjunction with XRD and Raman analysis to determine the phase formed.
REFERENCES


I. VISCOSITY, CRYSTALLIZATION AND GLASS-FORMING TENDENCY OF Na2O-CaO-B2O3 MELTS

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ABSTRACT

Melt properties and crystallization tendency for compositions in the Na2O-CaO-B2O3 system were characterized using differential thermal analysis and viscosity measurements. Characteristic viscosity (isokom) temperatures varied with the ratio between the modifier content (Na2O+CaO) and B2O3, particularly at lower temperatures, consistent with the changes in the relative concentrations of tetrahedral borons in the glass structure, determined by NMR spectroscopy. The melt fragility parameter followed a similar compositional dependence, consistent with reports in the literature relating this parameter to network topology. Glass stability parameters calculated from characteristic temperatures obtained by differential

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thermal analysis (DTA) indicate an increasing tendency towards crystallization with greater modifier contents, particularly for calcium-rich compositions.

**Keywords:** Viscosity, borates, glass, MYEGA

## 1. INTRODUCTION

Borate glasses have been developed for biomedical applications that benefit from their fast reaction kinetics in aqueous environments [1, 2]. In the presence of phosphate-containing solutions, including simulated body fluid, and under *in vivo* conditions, certain borate glasses convert to hydroxyapatite (HAp) more quickly than silicate bioactive glasses, and borate glasses are good hosts for ions that can promote healing [3].

Borate glasses that can be processed without crystallization are desired for a variety of biomedical applications. For example, one type of scaffold used for tissue engineering is made of fibers that are sintered by heating in a mold at a temperature between the glass transition temperature ($T_g$) and the onset of crystallization temperature ($T_x$) [2]. Fiber diameters can be controlled by the processing conditions and depend on the viscosity of the melt.
Unintentional crystallization makes it difficult to continuously pull fibers from a melt, and could lead to the formation of phases that are more difficult for the body to resorb [3]. In addition, a partially crystallized scaffold may have different mechanical properties that would limit its application.

The borate bioactive glasses that have received the most attention are borate analogs of two important silicate bioactive glass compositions, 45S5 Bioglass® [4] and 13-93 [5]. These compositions are based on the Na$_2$O-CaO-B$_2$O$_3$ glass-forming system, with other components added to optimize the melt and glass properties of the silicate analogs [6]. These borate compositions were not optimized for any particular property, but have been found in animal studies to promote the formation of new bone [3] and blood vessels [7, 8].

Donohoe, et al., [9] mapped out the glass forming region for the Na$_2$O-CaO-B$_2$O$_3$ system. In addition, they found that properties followed trends associated with the change in boron coordination. For example, $T_g$ increased with the additions of Na$_2$O and CaO to maximum values for compositions expected to have maximum fractions of four coordinated borons in their structures. Minimum values in the thermal expansion coefficients occurred for similar compositions. The compositions where these inflections in property
trends occurred depended on the B$_2$O$_3$ content, but glasses with more CaO had greater values for T$_g$ than Na$_2$O-rich compositions.

In the present study, the compositional dependence of the viscosity and crystallization behavior of melts and glasses in the Na$_2$O-CaO-B$_2$O$_3$ system are described, and property trends are related to structural changes in the borate network.

2. EXPERIMENTAL PROCEDURE

Glasses were prepared from batches of reagent grade Na$_2$CO$_3$, CaCO$_3$ and H$_3$BO$_3$ (Alfa Aesar, 99.5+). Each batch was melted for thirty minutes in a Pt-10Rh crucible between 800°C and 1100°C, depending on the composition, to produce melts that typically weighed 100 grams. Melts were poured onto a steel plate and glasses were annealed 5°C above their respective glass transition temperature (T$_g$) for four hours then cooled to room temperature at approximately 2°C/minute. All glasses were stored in a desiccator prior to characterization.

Representative glass compositions were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 2000 DV) and found to be within two mole percent of the nominal compositions. The nominal glass compositions are used throughout this paper.
Differential thermal analysis (DTA) measurements were made using a Perkin Elmer DTA 7. Experiments were run on 5-30 mg of glass powder, 75-150 µm in diameter, in alumina crucibles under nitrogen. Smaller sample masses were used for compositions that exhibited large heats of crystallization. A heating rate of 10°C/minute was used to determine $T_g$ (±2°C), the onset of crystallization, $T_x$ (±3°C), and the onset of melting, $T_m$ (±2°C). Heating rates of 5, 10, 15 and 20°C/minute were used to determine the liquidus temperature, following Ferreira’s method [10]. Liquidus temperatures were compared to those reported by Lawson [11] and confirmed by gradient furnace measurements using a modification of ASTM standard C829-81, where the temperature hold was one hour to minimize boron volitalization.

Viscosity measurements were made using the parallel plate viscometer (PPV) method and the rotating cylinder method. Cylindrical samples for the PPV study, ~5 mm in diameter and 5-6 mm in height, were core-drilled from the annealed cast glass samples and the cylinder ends were polished with 300-600 grit silicon carbide paper. A Perkin-Elmer DMA-7e was used to apply a static load of 200mN to a cylinder, which was then heated at rates between 2 and 10°C/min, depending on crystallization tendency. The cylinder deformation rate ($dh/dt$) was used to calculate the viscosity ($\eta$) over the range between
$10^6$ and $10^9$ Pa-s, following the method described by Rincon and Romero [12]. The isokom temperatures from the PPV tests were reproducible to ±7°C.

Viscosities in the range between $10^{-1}$ and $10^1$ Pa-s were obtained using the rotating cylinder method in two different configurations. In one test, a Brookfield DV-II viscometer was used with a platinum spindle and calibrated using Brookfield standard viscosity oils. Isothermal melt viscosities were measured on cooling at 25°C increments between about 1050°C and 800°C. Different rotational speeds were used at each temperature when possible. The platinum spindle was also used with a Haake ME1700 high temperature viscometer, calibrated using the NIST borosilicate reference glass, 717a. Isokom temperatures from the rotating spindle tests were reproducible to ±25°C.

A Bruker Avance II Spectrometer with a 14.1 Tesla/600MHz was used to collect $^{11}$B MAS NMR spectra that were recorded at a frequency of 192.54 MHz and a spinning rate of 12 kHz. The applied pulse length was 0.8 ms and a 2 s recycle delay was used. $\text{H}_3\text{BO}_3$ was used as the chemical shift reference. The ratio of the areas of peaks assigned to trigonal and tetrahedral borate sites was used to determine the fraction of $\text{BO}_4^-$ units ($\text{fBO}_4^-$).
3. RESULTS

The batched compositions of the Na$_2$O-CaO-B$_2$O$_3$ glasses that were prepared for this study, are shown in Figure 1, along with the glass-forming range reported by Donohoe and Shelby [9]. Glasses with more than 20 mole% CaO are of particular interest for biomedical applications because they most readily react with phosphate anions in the body to form hydroxyapatite, a component of bones [4].

Figure 2a shows DTA scans for the 22.5Na$_2$O-7.55CaO-70B$_2$O$_3$ glass, collected at different heating rates. Characteristic temperatures, $T_g$, $T_x$, and $T_m$ are indicated on the scan collected at 10°C/min. The offset temperatures for the melting peak, $T_{m,end}$, are also indicated on each of the scans collected at the different heating rates, and Figure 2b shows the dependence of $T_{m,end}$ on heating rate. According to Ferriera, et al., [10], extrapolating this trend to a heating rate of 0°C/min provides a measure of the liquidus temperature for a melt. The characteristic temperatures for each composition are given in Table I.

Figure 3 shows the viscosity data collected for $x$Na$_2$O-$xCaO$-(100-2$x$)B$_2$O$_3$ for $x$=5, 10 and 15. The viscosity measurements were fit using the MYEGA viscosity model [13]:
The fitting parameters are the melt fragility, $m$, glass transition temperature, $T_g$, defined as $\log \eta = 12$ (Pa s), and melt viscosity at infinite temperature, $\log_{10} \eta_\infty$. The fragility parameter is a measure of the temperature dependence of viscosity as a melt is cooled to the glass transition temperature ($T_g$) [14]. Figure 3 shows compositions with different MYEGA parameters. As $x$ increases, $m$ and $T_g$ both increase. The fitting parameters for the viscosity curves for every sample are also listed in Table I.

Examples of the compositional dependence of the isokom temperatures for Na-Ca-borate melts are shown in Figure 4. Figure 4a shows that for a series of glasses with a fixed $\text{Na}_2\text{O} : \text{CaO}$ ratio, the isokom temperatures go through a maximum near 30 mole% total modifying oxide ($\text{Na}_2\text{O} + \text{CaO}$). Similar trends have been reported for binary alkali borate melts [15, 16]. Figure 4b shows that replacing $\text{Na}_2\text{O}$ with $\text{CaO}$ in a series of glasses with a constant 65 mole % $\text{B}_2\text{O}_3$ content systematically increases the isokom temperatures.

The $^{11}\text{B}$ NMR spectra for the $x\text{Na}_2\text{O} - x\text{CaO} - (100 - 2x)\text{B}_2\text{O}_3$ glasses are shown in Figure 5a. The peak near 2ppm is due to four-coordinated boron and the broad band between 10-20ppm is due to

$$
\log_{10} \eta(T) = \log_{10} \eta_\infty + (12 - \log_{10} \eta_\infty) \frac{T_g}{T} \exp \left[ \left( \frac{m}{12 - \log_{10} \eta_\infty} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right]
$$

(1)
three-coordinated boron [17, 18]. The relative areas of these features indicate the fraction of boron sites with that coordination number. As the mole % of (Na₂O+CaO) increases, the fraction of four-coordinated boron (fBØ₄⁻) increases (Figure 5b).

4. DISCUSSION

4.1 Structure and Viscosity

When a modifying oxide is added to B₂O₃ glass, neutral trigonal sites (BØ₃) in the borate network are replaced by anionic tetrahedral sites (BØ₄⁻) [19]. Here, Ø represents an oxygen that links two neighboring B-polyhedra. Figure 5b shows that the fraction of tetrahedral borate sites, fBØ₄⁻, determined by ¹¹B NMR, increases systematically as the fraction of modifying oxide (Na₂O+CaO) increases for the Na₂O-CaO-B₂O₃ glasses. It is also interesting to note that for glasses with <70 mole% B₂O₃, those that are CaO-rich have greater values of fBØ₄⁻ than those that are Na₂O-rich, consistent with previous studies of binary borate glasses [20, 21].

The increase in the overall connectivity of the glass structures with increasing [Na₂O+CaO] helps explain the initial increase in the isokom temperatures, particularly at the lower temperatures, as shown in Figure 4a. The effect of total modifier content is less significant at lower viscosity (e.g., the 10² Pa-s isokom temperatures), and this is
related to the melt fragility, discussed below. For glasses with similar B$_2$O$_3$-contents and so similar values of fBØ$^-$ (Figure 5), shows that, with the exception of glasses with the lowest B$_2$O$_3$ contents, replacing Na$_2$O with CaO leads to a significant increase in the isokom temperatures (Figure 4b). This increase can be related to the greater field strength of the Ca$^{2+}$ ions compared to Na$^+$, and is consistent with the literature [22].

Figure 7 shows the NMR spectra for the xNa$_2$O-(35-x)CaO-65B$_2$O$_3$ glass series. There appears to be a shift to higher ppm in the location of the four-coordinated boron peak, centered on a chemical shift of 2ppm, with an increase in the amount of Na$_2$O. This is possibly due to increased numbers of three-coordinated boron connected to the four-coordinated boron [23]. There is also a change in the line shape for the three-coordinated boron peak. This indicates a change in the type of three-coordinated boron that is present in the glass structure. This change in type could be linked to either the number of NBO associated with the boron or if the boron is in a ring or chain formation [17]. These changes in both the three- and four-coordinated boron peaks indicate a difference in the super-structural units which might account for the change in the fBØ$^-$.  

Figure 6a shows the compositional dependence of the fragility parameter from the MYEGA fits of the viscosity measurements for the
Na$_2$O-CaO-B$_2$O$_3$ melts. In general, “m” increases with increasing [Na$_2$O+CaO], up to about 30 mole% modifying oxide (Figure 6b). Also plotted in Figure 6b are the fragility parameters for several series of binary alkali borate glasses [24] and fragility parameters predicted from topological constraint theory for Na$_2$O-CaO-B$_2$O$_3$ melts (gray boxes) by Smedskjaer, et al. [25]. There is good agreement between the results of the present study and those predicted by Smedskjaer et al. for compositions with [Na$_2$O+CaO] contents up to about 30 mole%. However, the present study shows a much more complicated dependence of the fragility parameter on the Na$_2$O:CaO ratio for melts with greater than 30 mole% [Na$_2$O+CaO] contents than is captured by the topological model. This compositional range is also where a maximum in the concentration of the fBØ$_4^-$ is found (Figure 5b), and where the modifier dependence of fBØ$_4^-$ at constant B$_2$O$_3$ content is most apparent.

4.2 Crystallization behavior and glass forming ability

There are at least two processing conditions relevant to the formation of biomedical scaffolds where the stability of a glass against crystallization must be considered. The first involves cooling a melt through the liquidus temperature to form a crystal-free glass. These conditions describe the glass forming ability (GFA) of the melt and
define the critical cooling rate (CCR) for glass formation. CCR is often
difficult to determine, especially for compositions that are slow to
crystallize [26, 27]. The second condition involves re-heating a glass
above the glass transition temperature, for example to sinter particles
or fibers, while avoiding crystallization; this is the crystallization
tendency of a glass. Both GFA and crystallization tendency depend on
the balance between the thermodynamic driving force and a kinetic
barrier for crystallization.

Several different parameters based on the characteristic
temperatures obtained from DTA/DSC measurements have been
developed to predict the glass forming ability and crystallization
tendency, including the Angell parameter [28] (Eq. 2), and the Hruby
parameter [29] (Eq. 3):

\[ K_A = (T_x - T_g) \]  
\( (2) \)

\[ K_H = (T_x - T_g) / (T_m - T_x) \]  
\( (3) \)

These parameters use the characteristic temperatures defined in
Figure 2a. The Angell parameter indicates the resistance of a glass to
crystallization on re-heating [30]; the larger the difference between \( T_g \)
and \( T_x \), the more stable the glass is against crystallization, an
indication of lower crystallization tendency. The temperature range defined by the Angell parameter is often used for sintering glass fibers and powders for biomedical scaffolds [1]. The term \((T_m - T_x)\) in the Hruby parameter is related to the glass forming ability of a melt; the smaller this term, the easier it will be to quench a melt and form a glass. As noted for the Angell parameter, a greater value of the Hruby parameter also indicates greater stability against crystallization upon re-heating.

Figure 8a and b show the compositional dependences of the Angell and Hruby parameters for the \(\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3\) system, respectively. Compositions that are most resistant to crystallization have \(\text{B}_2\text{O}_3\)-contents near 80 mole% and CaO-to-\(\text{Na}_2\text{O}\) ratios greater than one. In both figures, the compositions of known crystalline compounds [11] are also indicated, and it appears that melts with compositions near these compounds have lower stability parameters, compared to compositions further from the stoichiometric crystalline phases. This decrease in the glass stability parameters stems from how they are defined. The value of \((T_m - T_x)\) is roughly similar to the temperature range between the liquidus and the solidus temperatures. This means that the melt does not have a large range of temperatures where crystallization is likely to occur. Since glass is a metastable state linking the glass transition temperature is difficult but the \((T_x - T_g)\)
value is connected to the range over which the sample can be heated without crystallization which helps control the glass stability.

There is a thermal history dependence for crystallization tendency [31], and Zheng [32] noted this in a DSC study of the glass forming ability of the $\text{Na}_2\text{O}-\text{CaO-B}_2\text{O}_3$ system. Some glasses that crystallized in an initial DSC scan did not re-crystallize on subsequent heating after a melt and cooling cycle as well. This is why the glass stability parameters are not good indicators of glass forming ability. The crystallization behavior of the glass is dependent on the thermal history. This could be due either to a change in the boron coordination that decreases the likelihood of crystallization as suggested by Zheng [32] or a decrease in the number of nuclei in the glass after cooling from a melt. Cooling from a melt leaves a pristine surface. When glasses are crushed the imperfections in the surface and the accumulation of dust will act as nucleation sites [33]. The lower number of nuclei in glass after being cooled from a melt would cause the onset of the crystallization peak to shift to higher temperatures or not be large enough to measure.

The reduced glass transition temperature ($T_{rg} = T_g/T_{liq}$) has been used to indicate the glass forming ability of a melt, with greater values associated with better glass-forming tendency [34]. This is based on the observation that avoiding crystal formation when quenching a melt
from $T_{\text{liq}}$ to $T_g$ is easier when that temperature range is small. There is also a correlation between $T_{rg}$ and the tendency of a super-cooled liquid towards either surface or bulk nucleation. If $T_{rg}$ is greater than $\approx 0.58$, then the glass will display only surface nucleation within the laboratory time scale [26, 35, 36]. Based on this, better glass forming systems should form crystals mainly through surface nucleation.

The glasses in this system all have $T_{rg}>0.58$. This corresponds well with reports in the literature where pure $\text{B}_2\text{O}_3$ glasses have a $T_{rg}$ value of 0.75 and display only surface nucleation [26]. This is important because particles or fibers used to produce scaffolds can have surface nuclei due to grinding or degradation under ambient conditions which will provide a place for crystallization to begin. However, since these glasses do show surface nucleation, as seen from the reduced glass transition temperatures, it is likely that the surface after melting no longer has the concentration of nuclei needed to crystallize on reheating. This indicates that the glass stability parameters will change with the surface area of the specimen used in the DTA measurement and that it will be less likely to correspond to the glass forming ability since that is typically of interest on cooling rather than heating.

The glass forming ability of a melt indicates how quickly the melt needs to be cooled to form a crystal-free glass. One way to understand
glass forming ability is to consider crystallization kinetics. The relationships between viscosity and characteristic temperatures related to crystallization can be used to predict the glass forming ability of a melt. Melts that are more viscous at their liquidus temperatures crystallize more slowly on cooling and will thus form a glass more readily as crystallization is hindered by slower diffusion [37, 38]. The viscosity of the melt at the liquidus temperature is shown in Figure 9a. By this measure, the composition with the best glass forming ability (highest viscosity at the liquidus temperature) is 7.5Na$_2$O-22.5CaO-70B$_2$O$_3$ (log $\eta_{\text{liq}}$=1.65 Pa-s), and the composition with the poorest glass forming ability (lowest viscosity at the liquidus temperature) is 10Na$_2$O-30CaO-70.0B$_2$O$_3$ (log $\eta_{\text{liq}}$=-0.98 Pa-s).

Also important to glass formation is how rapidly the viscosity changes as it cools. In less viscous melts, a rapidly increasing viscosity through the liquidus temperature upon cooling may more readily avoid crystallization. Melt fragility describes how rapidly the viscosity changes at $T_g$, but no correlation was between fragility and the critical cooling rate of Na-Ca-borate melts [32]. However, a rapid change in viscosity near the liquidus temperature may be a better indication of glass forming tendency. The change in the viscosity at the liquidus temperature, $(d\eta/dT)_{T_{\text{liq}}}$, was calculated based on the the derivative of MYEGA model, and the results are shown in Figure 9b.
The region near 30CaO-70B₂O₃ has both a greater viscosity at \(T_{\text{liq}}\) and a more rapid change in viscosity, indicating an increased glass forming ability. Similarly, the melts near 10Na₂O-30CaO-60B₂O₃ have both a lower viscosity at \(T_{\text{liq}}\) and a slower change in the viscosity at the liquidus temperature and would have a decreased glass forming ability. However, neither the viscosity at the liquidus temperature nor the change in the viscosity at the liquidus temperature tells the whole story. The interdependence between these parameters becomes complicated near the composition 17.5Na₂O-17.5CaO-65B₂O₃ where there is a relatively low viscosity but a relatively large change in the viscosity at the liquidus temperature. The prediction for GFA based on the viscosity at the liquidus temperature and the GFA based on the change in the viscosity contradict each other and since the overall importance of one factor compared to the other is unknown, an estimate of the glass forming ability is difficult to quantify.

5. CONCLUSIONS

The compositional dependence of isokom temperatures for melts in the Na₂O-CaO-B₂O₃ system depend on the boron coordination number and the Na₂O:CaO ratio. Glasses with greater average connectivity in the
borate network and with lower Na₂O:CaO ratios have greater isokom temperatures.

Glasses with the best stability against crystallization, defined by the relationships between Tₓ, Tₓ, and Tₓ, have compositions near 5Na₂O-15CaO-80B₂O₃ and glass stability decreases near the compositions of stoichiometric crystalline compounds.

The greater the glass forming ability for the glass system, the less likely the melt is to crystallize on cooling. Based on the glass forming ability as well as the glass stability, compositions with 65-70 mole% B₂O₃ and CaO>Na₂O should resist crystallization during conventional processing.
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Figure 1: Glass forming region based on Donohoe [9]. Horizontal lines represent compositions that crystallized and diagonal lines indicate compositions that phase separate. Blue squares indicate the batched compositions of homogeneous glasses made in this study, stars are crystallized samples, open boxes are phase-separated samples.
Figure 2: Ferriera’s DTA method [10] for determining the liquidus temperature for a melt is illustrated for the 22.5Na₂O-7.5CaO-67.0B₂O₃ composition; a) the DTA data collected at different heating rates; b) the melt peak offset temperature (Tₘ,end) for different heating rates. The liquidus temperature is the y-intercept.
Figure 3: Viscosity curve for \( x\text{Na}_2\text{O}-x\text{CaO}-\text{(100-2x)}\text{B}_2\text{O}_3 \) (\( x=5, 10 \) or 15) glass with the PPV and rotating spindle data (symbols) fit (line) by the MYEGA model [13], Eq. 1.
Figure 4: Isokom temperatures [log viscosity=2(●), 7(■) and 12(▲)]
a) xNa₂O-xCaO-(100-2x)B₂O₃ glasses, and b)(35-x)Na₂O-xCaO-65B₂O₃ glasses.
Figure 5: a) The $^{11}$B NMR spectra for the $x$Na$_2$O-$x$CaO-(100-2x)B$_2$O$_3$ glasses and b) the fraction of 4-coordinated boron for glasses in the Na$_2$O-CaO-B$_2$O$_3$ system based on the NMR spectra.
Figure 6: a) The fragility parameter for melts in the Na$_2$O-CaO-B$_2$O$_3$ system, from the MYEGA fits to the viscosity data, and b) fragility parameters from the present study (open symbols) compared with those reported for binary borate melts (closed symbols [23]) and predicted from a topological model (gray boxes [25]).
Figure 7: $^{11}$B NMR spectra for the $x$Na$_2$O-(35-$x$)CaO-65B$_2$O$_3$ glass series.
Figure 8: Glass stability parameters for the Na$_2$O-CaO-B$_2$O$_3$ system, a) Angell parameter (Eq. 2), and b) Hruby parameter (Eq. 3); the compositions of stable compounds are indicated by the black squares).
Figure 9: Kinetic analyses for glass forming ability in the Na$_2$O-CaO-B$_2$O$_3$ system, a) log viscosity (Pa·s) at the liquidus temperature; b) (dη/dT)$_{T_{liq}}$. 
Table I: Characteristic temperatures from DTA measurements and parameters from fitting viscosity to the MYEGA equation.

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<th>Composition</th>
<th>$T_g$ (°C)</th>
<th>$T_x$ (°C) (1$^{st}$ onset)</th>
<th>$T_m$ (°C) (1$^{st}$ onset)</th>
<th>$T_m$ (end) (°C)</th>
<th>$T_g$ (°C)</th>
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II. SPECTROSCOPIC STUDY OF THE STRUCTURE OF TERNARY ALKALI-ALKALINE EARTH-BORATE GLASSES

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ABSTRACT

The structure of glasses in the 10R₂O-10R’O-80B₂O₃, 10Na₂O-10BaO-80B₂O₃, and xR₂O-xCaO-(100-2x)B₂O₃ systems (R=Li, Na or K, R’=Mg, Ca or Sr, and x=10, 15 or 20) were studied using Raman and ¹¹B MAS-NMR spectroscopies. Increasing the total modifying oxide content of the glasses changes the fraction of tetrahedral borate sites (fBØ₄⁻) in a way that can be generally predicted from simple empirical models developed for binary borate glasses; however, there are some structural trends that depend on the type of modifying cation. 10R₂O-10R’O-80B₂O₃ glasses with larger alkali or alkaline earth cations have fewer boroxol rings and the MgO-containing glasses have lower fBØ₄⁻ (25%) than CaO- and SrO-doped glasses (30%). Similar decreases in fBØ₄⁻ are noted for MgO-containing 15Na₂O-15R’O-70B₂O₃ and

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20Na₂O-20R’O-60B₂O₃ glasses. Structural reactions that explain these trends are discussed.

**Keywords:** glass, Raman, borate structure

### 1. INTRODUCTION

Alkali-alkaline earth borate glasses are being developed for biomedical applications [1-3]. When exposed to phosphate containing solutions, under in vitro and in vivo conditions, these glasses convert to bio-compatible hydroxyapatite and so show promise as scaffold materials for bone defects [4]. Other compositions promote healing of soft tissue wounds [5].

In order to tailor the properties of these glasses, an understanding of the relationships between composition and structure is desired. Much is known about the relationships between the compositions and structures of binary alkali and alkaline earth borate glasses, with $^{11}$B nuclear magnetic resonance (NMR) spectroscopy providing detailed information about the compositional dependences of the trigonal and tetrahedral sites that constitute the borate network structures [6, 7], and Raman spectroscopy providing useful information about the super-structural units, including rings, that form
from the polyhedral units [8-11]. Quantitative models have been developed to explain the effects of composition on boron coordination numbers in the binary systems, but such models have not been systematically applied to the ternary alkali-alkaline earth borate glasses, nor has there been a systematic examination of the effects of different alkali and alkaline earth ions on ternary borate glass structures.

In this paper, the structures of several series of ternary alkali-alkaline earth borate glasses are described using quantitative and qualitative information from $^{11}\text{B}$ NMR and Raman spectroscopies. The effects of both total modifying oxide content and the types of different modifying oxides on the borate network are described, including Na-Ca-borate glass compositions that form the bases for some of the new borate biomedical glasses.

2. EXPERIMENTAL PROCEDURE

Eighteen glasses in the 10R$_2$O-10R’O-80B$_2$O$_3$ and xNa$_2$O-xR’O-(100-2x)B$_2$O$_3$ systems (R=Li, Na or K, R’=Mg, Ca or Sr (Ba included in second series) and x=10, 15 or 20, with a 5Na$_2$O-5CaO-90B$_2$O$_3$ glass included) were batched to yield 100 grams of glass, using reagent grade carbonates and boric acid ($\text{H}_3\text{BO}_3$, Li$_2$CO$_3$, Na$_2$CO$_3$, K$_2$CO$_3$,}
MgCO$_3$, CaCO$_3$, SrCO$_3$ and BaCO$_3$ from Alfa Aesar). Batches were mixed and then melted in a platinum-rhodium crucible at 800-1100°C based on the composition. The melts were poured on a steel plate and allowed to cool.

Glass powders (75-150 µm) were dissolved in deionized water and the glass compositions were determined using a Perkin Elmer Optima 2000 inductively couple plasma-optical emission spectroscopy (ICP-OES). The glass compositions were found to be close (±1.5 mole% for R$_2$O or R’O and ±3 mole% for B$_2$O$_3$) to the nominal compositions based on ICP-OES measurements. Nominal compositions are used to denote the glasses, but the analyzed compositions are used in all discussions.

The structures of the glasses were characterized using Raman spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Raman spectroscopy was done using a Reinshaw inVia with a 488nm Ar$^+$ laser, calibrated using an internal silicon reference, for 200-2000cm$^{-1}$. A Bruker Avance II Spectrometer with a 14.1 Tesla/600MHz field was used to collect $^{11}$B MAS NMR spectra that were recorded at a frequency of 192.54 MHz and a spinning rate of 12 kHz. The applied pulse length was 0.8 ms and a 2 s recycle delay with a small tipping angle to enable quantification of boron species was used. Chemical shifts were referenced to boric acid with borax as a
secondary reference. The ratio of the areas of peaks assigned to
trigonal and tetrahedral borate units, including the first set of high and
low frequency spinning side bands, were used to determine the
fraction of BØ₄⁻ units.

3. RESULTS

3.1 NMR Spectra

The $^{11}$B NMR spectra for the xNa₂O-xCaO-(100-2x)B₂O₃ glasses
are shown in Figure 1. The more symmetric peak located at a chemical
shift of approximately 2ppm indicates four-coordinated borate units
and the broader, asymmetric peak between 10 and 20ppm is due to
three coordinated borate units [12]. The relative areas of these peaks
can be used to quantify the relative amounts of each type of unit.
Thus, as shown in Figure 2, the increase in the relative intensity of the
2ppm peak with increasing modifier content indicates an increase in
the fraction of four coordinated borons in the glass network, fBØ₄⁻.
(Here, Ø indicates a bridging oxygen that links neighboring borate
polyhedra.) Similar compositional trends are well documented for
binary borate systems [6, 13-15].
Figure 1: $^{11}$B NMR spectra for the xNa$_2$O-xCaO-(100-2x)B$_2$O$_3$ glass series; spectra are normalized to the total spectral area.

Figure 2: The fraction of four-coordinated boron in the glasses in the xNa$_2$O-xR'O-(100-2x)B$_2$O$_3$ series, where R'=Mg, Ca, Sr or Ba. The dotted lines are the predicted fBØ$_4$ from Eq. 1 (up to 33 mole % modifier) and Eq 2 (>33 mole% modifier).

Figure 3 shows the $^{11}$B NMR spectra of the 10R$_2$O-10R'O-80B$_2$O$_3$ glasses. The relative intensity of the peak at 2ppm due to BØ$_4$ units is lower for the MgO-containing glasses than for the CaO- and SrO-containing glasses, indicating that the fraction of tetrahedral borate units in the MgO-containing glasses is about 25%, compared to 28-
30% for the other two sets of glasses (Figure 3c). Figure 2 shows that there are systematically fewer tetrahedral borate sites in the MgO-containing 15Na₂O-15R’O-70B₂O₃ and 20Na₂O-20R’O-60B₂O₃ glasses, as well.

Figure 3: a) The NMR spectra for the 10K₂O-10R’O-80B₂O₃ glasses, b) NMR spectra for the 10R₂O-10CaO-80B₂O₃ glasses, and c) fraction of four-coordinated boron for each composition in the 10R₂O-10R’O-80B₂O₃ glass series, where R=Li, Na, or K, and R’=Mg, Ca or Sr.
3.2 Raman Spectra

The Raman spectra for glasses in the xNa$_2$O-xCaO-(100-2x)B$_2$O$_3$ series are shown in Figure 4. The spectra from glasses with less than about 30 mole% modifiers (x<15) have two sharp peaks centered at 806 cm$^{-1}$ and 775 cm$^{-1}$ that change in relative intensity with composition. The peak at 806 cm$^{-1}$ has been assigned to the breathing mode for planar six-membered boroxol rings formed by three BØ$_3$ triangles$^{10;12}$. The peak at 775 cm$^{-1}$ has been assigned to the symmetric breathing mode for a six-membered ring containing where one BØ$_3$ triangle is replaced by a BØ$_4$ tetrahedron. These rings are shown schematically in Figure 4. The boroxol ring peak decreases in relative intensity with increasing modifying oxide content (xNa$_2$O+xCaO), and has disappeared from the spectrum of the x=15 glass. The intensity of the peak at 775 cm$^{-1}$ increases relative to the boroxol ring peak with increasing total modifier content, consistent with the increase in fBØ$_4^-$ determined from the $^{11}$B NMR spectra of the same glasses (Figure 2). In addition, this peak becomes broader and shifts to lower wavenumbers with increasing modifier content, from
about 777 cm\(^{-1}\) (x=5) to about 765 cm\(^{-1}\) (x=20). These changes in the spectral features are consistent with the replacement of B\(\bar{\text{O}}_3\) triangles by B\(\bar{\text{O}}_4^-\) tetrahedra in the rings, including the formation of other superstructural units like the diborate group shown in Figure 4 [9, 10]. Other borate structures with B\(\bar{\text{O}}_4^-\) tetrahedra account for the lower intensity bands near 520, 940 and 1120 cm\(^{-1}\) [10, 16].

The broad peaks in the Raman spectra from the xNa\(_2\)O-xCaO-(100-2x) B\(_2\)O\(_3\) glasses in the 1200-1550 cm\(^{-1}\) range are associated with non-bridging oxygens on metaborate triangles, B\(\bar{\text{O}}_2\)O\(^-\) [11]. These units are present in glasses with x=5, but become significant for x\(\geq\)15.

![Raman Spectra](image)

Figure 4: Raman spectra for the glasses in the xNa\(_2\)O-xCaO-(100-2x) B\(_2\)O\(_3\) series.

Figure 5a shows the Raman spectra for the 10R\(_2\)O-10CaO-80B\(_2\)O\(_3\) glasses and Figure 5b shows the Raman spectra for the 10K\(_2\)O-10R'\(\text{O}\)-80B\(_2\)O\(_3\) glasses. In both series, the area of the tetrahedrally-
modified ring peak at 775 cm\(^{-1}\) increases relative to the area of the boroxol ring peak at 803 cm\(^{-1}\), in the order of increasing modifier size, Li>Na>K and Mg>Ca>Sr, respectively. In addition, there are small shifts to lower wavenumbers for the tetrahedrally-modified ring peak with larger modifier sizes. Both trends indicate that may be more B\(\bar{O}_4^–\) units in glasses with larger cations.

Figure 5: Raman spectra for a) the 10R\(_2\)O-10CaO-80B\(_2\)O\(_3\) glasses, and b) the 10K\(_2\)O-10R\(^I\)O-80B\(_2\)O\(_3\) glasses.

4. DISCUSSION

Studies of binary alkali or alkaline earth borate glasses show that the additions of modifying oxides to B\(_2\)O\(_3\) convert three-coordinated, trigonal borate units (B\(\bar{O}_3\)) to four-coordinated, tetrahedral borate units (B\(\bar{O}_4^–\)) [14]. The increase in the connectivity of the borate network accounts for the initial increase in glass transition temperature (T\(_g\)) and decrease in CTE [17, 18] when modifying oxides
are added. After the modifier concentration reaches approximately 33 mole %, these property trends often reverse because the further addition of modifying oxides will cause the conversion of BØ₃ and BØ₄⁻ units to three-coordinated borate units now with nonbridging oxygens (NBO), BØ₂O⁻ or BØO₂⁻ [19]. Empirical models have been developed to describe the compositional-dependence of the fraction of BØ₄⁻ units (fBØ₄⁻) in a glass. For glasses with the general molar composition xR₂O-(100-x)B₂O₃, Eq. 1 describes the compositional dependence of fBØ₄⁻ for compositions in the range 0<x<33.3, and Eq. 2, describes the compositional dependence of fBØ₄⁻ for compositions in the range x>33.3 [15].

$$f_{B\theta_4^-} = \frac{x}{100-x}$$  \hspace{1cm} (1)

$$f_{B\theta_4^-} = \frac{300-4x}{500-5x}$$  \hspace{1cm} (2)

These two relationships are plotted with the quantitative NMR analyses of fBØ₄⁻ in Figure 2, where they well describe the overall compositional dependence of the concentration of tetrahedral sites. Accompanying this increase in fBØ₄⁻, at least up to a total modifier content of around 30 mol%, is a change in the dominant super-structural unit detected in the Raman spectra (e.g., Figure 4), from
boroxol rings, designated as \((\text{B}_3\text{O}_{4.5})\), to a tetrahedrally-modified ring, designated as \((\text{B}_3\text{O}_5^-)\) and represented by:

\[
2(\text{B}_3\text{O}_{4.5}) + \text{R}_2\text{O} \rightarrow 2(\text{B}_3\text{O}_5^-) \cdot 2\text{R}^+
\]  (3)

Shifts in the positions of the dominant Raman peak indicate that with further additions of modifying oxide, additional tetrahedra can be incorporated into these super-structural units, like the diborate unit \((\text{B}_4\text{O}_7^{2-})\) illustrated in Figure 1:

\[
4(\text{B}_3\text{O}_5^-) \cdot 4\text{R}^+ + \text{R}_2\text{O} \rightarrow 3(\text{B}_4\text{O}_7^{2-}) \cdot 6\text{R}^+
\]  (4)

Above about 30 mol\% modifying oxide, \(\text{fB}\text{O}_4^-\) decreases, to be replaced by three-coordinated borate units now with non-bridging oxygens (NBO), \(\text{B}\text{O}_2\text{O}^-\) or \(\text{B}\text{O}_2\text{O}^-\)\(\text{[19]}\). It is possible that tetrahedra-containing rings like the dibo rates are replaced by anionic rings of trigonal borates, like the metaborate anion \((\text{B}_3\text{O}_6^{3-})\):

\[
3(\text{B}_4\text{O}_7^{2-}) \cdot 6\text{R}^+ + 3\text{R}_2\text{O} \rightarrow 4(\text{B}_3\text{O}_6^{3-}) \cdot 12\text{R}^+
\]  (5)

The increase in the relative intensity of the Raman peaks in the range 1200-1500 cm\(^{-1}\) is consistent with an increase in the
concentration of trigonal borates with nonbridging oxygens in glasses with >30mol% modifying oxide.

However, the simple description of the structural changes implied by Eqs. (1-5) does not account for the systematic deviations that occur with different alkali and alkaline earth oxides in these glasses. For example, a consistently lower fraction of tetrahedral borons were found by NMR in the MgO-containing glasses (Figure 2), and the relative intensity of the Raman peak due to the boroxol rings decreases in the order of modifier size, for both alkali and alkaline earth ions (Figure 5). Similar observations have been made in previous studies of binary borate glasses where increasing the size of the alkali [20] or alkaline earth [11] modifying ion increases the fraction of tetrahedral borates (fBÖ4) in the network structure. In particular, Kamitsos, et al. have shown that MgO-containing borate glasses retain larger fractions of boroxol rings, and smaller fractions of diborate rings, than other alkaline earth containing borate glasses [8, 11, 21]. Such observations may be described by site disproportionation reactions like the following:

\[
(B_4O_7)^{2-} \cdot R^{2+} \leftrightarrow (B_3O_4.5) + (BØO^-) \cdot R^{2+}
\]  

(6)
Here, a diborate ring charge balanced by an alkaline earth cation (left) may be replaced by a neutral boroxol ring and an anionic borate triangle (right).

A related reaction involves the conversion of pentaborate anions \((B_5O_{13}^-)\) to boroxol rings and a metaborate anion:

\[
3(B_5O_{13}^-) \cdot 3R^+ \leftrightarrow 4(B_3O_{4.5}) + (B_3O_6^{3-}) \cdot 3R^+ \quad (7)
\]

Wu has proposed [22] that smaller and more highly charged cations, like \(Mg^{2+}\), prefer anions with more localized negative charge, like the non-bridging oxygens associated with the anions on the right of reactions (6) and (7). Larger cations, on the other hand, stabilize larger anions with more diffuse negative charge, like the diborate anion on the left of reaction (6) and the pentaborate on the left of reaction (7). If so, then such disproportionation reactions explain the trends in both the NMR and Raman spectra which indicate a preference for boroxol rings and anionic trigonal sites, particularly in the Mg-containing glasses.

The effect of alkali size on the NMR and Raman spectra of the 10R₂O-10CaO-80B₂O₃ glasses are interesting. The NMR results show a small, but systematic decrease in \(fB\) in the order Li>Na>K (Figure 3c) whereas the Raman spectra show an increase in the relative
intensity of the peak at 775 cm\(^{-1}\) assigned to the tetrahedrally-modified ring (Figure 5a) in the same alkali order. These are not necessarily contradictory results. The more intense 775 cm\(^{-1}\) Raman peak may not be due to relatively more tetrahedral sites with increasing alkali size, but instead may be due to a smaller concentration of boroxol rings associated with the 806 cm\(^{-1}\) peak. If more neutral borate triangles (BØ\(_3\)) are associated with structural motifs other than boroxol rings, then the relative intensity of the 775 cm\(^{-1}\) Raman peak will increase. Youngman and Zwanziger [16] propose that a greater fraction of “loose” BØ\(_3\) units constitute the structures of alkali borate glasses than BØ\(_3\) units in boroxol rings. Thus, if a greater fraction of “loose” BØ\(_3\) units are present in the structure of the 10K\(_2\)O-10CaO-80B\(_2\)O\(_3\) glass than in the 10Li\(_2\)O-10CaO-80B\(_2\)O\(_3\) glass, the boroxol ring Raman peak intensity will decrease and the relative intensity of the 775 cm\(^{-1}\) Raman peak for the K-glass would be greater than for the Li-glass, even though the former has a smaller fraction of tetrahedral sites (by NMR).

**5. CONCLUSIONS**

Compositional trends in the network structures of ternary alkali-alkaline earth borate glasses are similar to those reported for binary alkali and alkaline earth borate systems. \(^{11}\)B NMR indicates that, in
general, the compositional dependence of the fraction of tetrahedral network sites is consistent with empirical models developed for the borate glasses. Raman spectroscopy shows that trigonal and tetrahedral units form well-known super-structural rings, with the fraction of boroxol rings decreasing and the fraction of tetrahedrally-modified rings increasing with total modifier oxide content.

There are some structural features that depend not only on the total modifier content, but also on the type of modifier. For the 10K₂O-10R’O-80B₂O₃ series, there are fewer tetrahedral borates for the MgO glass than for the CaO and SrO glasses, indicating that more anionic triangular sites must be present in the MgO-glasses. Changing the type of modifier also affects the distributions of triangles and tetrahedra that form rings and other structural motifs. For example, the relative numbers of boroxol rings in 10R₂O-10R’O-80B₂O₃ glasses decrease with increasing size of both the alkali and alkaline earth modifying cation. The structural reactions that account for these differences must be considered before a detailed description of the relationships between the compositions, properties and structures of these glasses is developed.
ACKNOWLEDGEMENTS

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III. DISSOLUTION BEHAVIOR OF TERNARY ALKALI-
ALKALINE EARTH-BORATE GLASSES

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ABSTRACT

The dissolution processes of ternary alkali-alkaline earth borate
glasses in water were characterized. These glasses dissolve
congruently and the dissolution kinetics were linear, following the
contracting volume model for spherical particles. The dissolution rates
were dependent on the glass structure, with slower rates associated
with greater fractions of four-coordinated boron. For glasses with a
fixed alkaline earth identity, the dissolution rates increased in the
order Li<Na<K. For glasses with a constant alkali identity, the
dissolution rates increased in the order Ca<Sr<Mg. The effects of
different alkali and alkaline earth oxides on dissolution rates are

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Email: brow@mst.edu
discussed in terms of competing effects of four-coordinated boron and the field strength of the modifying cation.

**Keywords**: borate dissolution, hydrolysis

### 1. INTRODUCTION

Borate glasses in general are more reactive in aqueous environments than silicate glasses. This fast reactivity can be an advantage in many biomedical applications where tailored ion release rates are desired [1].

The processes by which glasses react in an aqueous solution include hydrolysis, hydration, and ion exchange [2]. Hydrolysis is the process where water reacts with the bridging oxygen that links two glass-forming polyhedra to form two hydroxyl bonds and so breakdown the glass network. Hydration is a similar process that affects the bonds between modifying metal polyhedra and glass-forming polyhedra to form hydrated modifying ions. Ion exchange is a process by which modifying metal ions in a glass structure are replaced by protons (or hydronium ions) as a result of the hydration reactions, leading to the selective leaching of mobile metal ions from the glass into the solution. Ion exchange reactions dominate the initial dissolution processes of alkali-containing silicate glasses in acidic and
neutral conditions, and are a transport-limited process, whereas the hydrolysis processes often exhibit reaction-controlled kinetics. These different reactions are coupled and all can contribute to the dissolution of a glass [2].

One other difference between silicate and borate glasses is how the addition of modifying oxides affect the structure of the glass. When modifying oxides are added to SiO$_2$, bridging Si-O-Si bonds are replaced by non-bridging oxygens (NBO). This will cause the network to dissolve faster because fewer bridging oxygens must be hydrolyzed to release a silicate anion. The addition of modifying oxides to B$_2$O$_3$, however, causes the boron coordination number to increase from three to four [3], and the greater number of structural cross-links has been associated with lower aqueous dissolution rates [4].

The identity of the alkali in binary borate glasses will also affect the dissolution rate of the glass. Zhang [5] found that larger alkali ions cause an increase in the dissolution rate and El-Alaily [6] report similar trends for divalent cations.

The aqueous dissolution rate is one of the factors that determine the bioactive response of a glass. Different dissolution rates may be required for different applications; e.g. slower rates for bone repair scaffolds versus soft tissue healing [7, 8]. Knowing the effects that composition, including the use of different alkali and alkaline earth
oxides, has on the dissolution mechanism and kinetics will useful in the design of new glasses for biomedical applications.

2. PROCEDURE

Fifteen glasses in the $10R_2O-10R'O-80B_2O_3$ and $xR_2O-xCaO-(100-2x)B_2O_3$ systems (R=Li, Na or K, R’=Mg, Ca, or Sr and $x=10, 15$ or 20) in addition to $5Na_2O-5CaO-90B_2O_3$, were batched using reagent grade carbonates and boric acid ($H_3BO_3$, $Li_2CO_3$, $Na_2CO_3$, $K_2CO_3$, $MgCO_3$, $CaCO_3$, and $SrCO_3$). Batches were melted in a platinum-rhodium crucible at 800-1100°C based on the composition. Glass compositions were determined using a Perkin Elmer Optima 2000 inductively couple plasma-optical emission spectrometer (ICP-OES). Compositions were within 3 mole % of the batched values, and all analyses are based on the analyzed compositions.

The density of each glass was measured in triplicate in deionized water using the Archimedes method. Glass samples were crushed and sieved to 75-150 µm powder. Powders were rinsed with ethanol through the 75µm sieve to remove fines. Sample powders were weighed and 150mg were placed in a 45µm mesh nylon bag, also washed with ethanol, and sealed using a butane torch. Bags were placed in 50mL of deionized water and placed in a shaking water bath
at 37ºC. Samples were run in triplicate. Ion concentrations for each element were measured using ICP-OES after different time increments, up to 24 hours for the 80 mole% B₂O₃ series and up to 168 hours for the glasses containing 60 or 70 mole% B₂O₃. After each dissolution time increment, the bags were removed from the water and dried in a 60 ºC drying oven overnight before re-measuring the mass. The final pH of the solutions was measured at room temperature using an Accumet pH electrode.

3. RESULTS

3.1 Glass Compositions

The analyzed glass compositions were similar to the nominal compositions (The densities of each glass are also given in Table I, along with the fractions of tetrahedral borate units, reported Goetschius et al. [9].)

Table I), where specific glasses are designated by their nominal compositions; e.g., 10Li10Mg80B designates the glass with the nominal molar composition 10Li₂O-10MgO-80B₂O₃. The densities of each glass are also given in Table I, along with the fractions of tetrahedral borate units, reported Goetschius et al. [9].
Table I: Analyzed compositions, in mole %, densities, and fractions of tetrahedral borate units [9] of the glasses with the designated molar compositions.

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<th>R’O (mole%)</th>
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<td>2.305</td>
<td>0.29</td>
</tr>
<tr>
<td>15Na15Ca70B</td>
<td>16.4</td>
<td>16.6</td>
<td>67.0</td>
<td>2.404</td>
<td>0.46</td>
</tr>
<tr>
<td>20Na20Ca60B</td>
<td>19.0</td>
<td>19.8</td>
<td>61.2</td>
<td>2.500</td>
<td>0.48</td>
</tr>
<tr>
<td>15Li15Ca70B</td>
<td>16.1</td>
<td>16.2</td>
<td>67.7</td>
<td>2.371</td>
<td>-</td>
</tr>
<tr>
<td>20Li20Ca60B</td>
<td>20.6</td>
<td>20.1</td>
<td>59.2</td>
<td>2.488</td>
<td>-</td>
</tr>
<tr>
<td>15K15Ca70B</td>
<td>13.8</td>
<td>14.9</td>
<td>71.4</td>
<td>2.327</td>
<td>-</td>
</tr>
<tr>
<td>20K20Ca60B</td>
<td>18.2</td>
<td>19.7</td>
<td>62.1</td>
<td>2.385</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Glass reaction in water

As the glasses dissolve in water the total weight of the glass present in the mesh decreases. Figure 1 shows the weight loss of the xK₂O-xCaO-(100-2x)B₂O₃ series fit using the CVM.
Figure 1: Weight loss data for glasses in the xK$_2$O-xCaO-(100-2x)B$_2$O$_3$ series.

The ion release data for the 15K$_2$O-15CaO-70B$_2$O$_3$ glass in water are shown in Figure 2. The horizontal dotted lines in Figure 2a are the respective concentrations of each element assuming complete dissolution, and the horizontal lines in Figure 2b are the analyzed ion ratios in the bulk glasses. These data are representative of the dissolution behavior of the other glasses studied.
Figure 2: Dissolution data for the 15K$_2$O-15CaO-70B$_2$O$_3$ glass in water; a) ion release data where the horizontal dotted lines indicate the respective concentrations assuming complete dissolution of the sample and the solid lines are the CMV fit for each ion; and b) the modifier ion concentration relative to boron concentration in solution or the course of the dissolution experiment.

For the 15K$_2$O-15CaO-70B$_2$O$_3$ glass in Figure 2, dissolution is complete after approximately 48 hours in water. The concentrations of the modifiers, K and Ca, relative to the boron concentration, Figure 2b, are constant with time. This means that these modifying ions are being released at the same rate as the network former is being released and therefore, the glasses are dissolving congruently.

The ion release and the weight loss data were fit using the contracting volume dissolution model (CVM) for a sphere [10] (Eq.1) to determine the reaction rate constant ($k_t$),

$$k_t = 1 - (1 - a)^{1/3} \quad (1)$$
where \( t \) is time, and \( \alpha \) is the fraction of sample dissolved. For the weight loss measurements, \( \alpha = (\text{weight lost/initial weight}) \), and assumes that no precipitation reactions are affecting the weight changes. For the ion release measurements, \( \alpha \) is the amount of an ion in solution divided by the total amount of that ion in the initial sample.

The weight loss data, Figure 1, and the ion release data from Figure 2 for the 15K\(_2\)O-15CaO-70B\(_2\)O\(_3\) glass were each fit using the CVM, as shown in Figure 3. The reaction rates for each data set, determined from the slopes of these plots and shown in the figure legend, are within the error bars shown in Figure 3.

![Figure 3: Boron, calcium and potassium ion release data and weight loss data from the 15K\(_2\)O-15CaO-70B\(_2\)O\(_3\) glass, each fit to the CVM. Dotted lines represent linear fits with a y-intercept of zero. Reaction rates for each data sets are reported with the respective legends.](image)

Additional examples of the CVM fits to weight loss data are shown in Figure 4 for the 10Na\(_2\)O-10R’O-80B\(_2\)O\(_3\) series of glasses.
Greater slopes indicate faster glass dissolution rates, and so for these glasses, the dissolution rate constant increases in the order Ca<Sr<Mg.

![Graph](image)

Figure 4: Weight loss data for the $10\text{Na}_2\text{O}-10\text{R'O}-80\text{B}_2\text{O}_3$ glass series, fit to the CVM; $\text{R'}=\text{Mg}, \text{Ca}, \text{or Sr}$.

The dissolution rates determined from the boron release measurements ($k\ (\text{ICP})$) agree very well with those calculated from the weight loss measurements ($k\ (\Delta w)$), as shown in Figure 5. Since the reaction rates were similar regardless of the measurement method, the boron release data is used for the reaction kinetics studies that follow.
Figure 5: CVM reaction rate constants calculated from weight loss and boron release measurements. The dashed line assumes that $k_{\text{ICP}} = k_{\Delta w}$.

The dissolution rates varied with the type of alkali and alkaline earth oxide added to the glass, as shown in Figure 6.

Figure 6: CVM reaction rate constants from the boron ion release data for the $10R_2O-10R'O-80B_2O_3$ glasses.
Table II lists the CVM reaction rates in 37°C water for each of the glasses studied here. Also listed are the pH values of the solutions after complete dissolution, and these values are plotted as a function of the total modifier content in Figure 7. The pH of the solution did not vary significantly with the identity of the modifying ion, but did depend on the overall concentrations of the modifier oxides in the glasses.

**Table II: CVM dissolution rates (from B-release data) and solution pH values after complete dissolution.**

<table>
<thead>
<tr>
<th>Glass Designation</th>
<th>k (ICP B), hr⁻¹</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Li10Mg80B</td>
<td>0.088</td>
<td>8.44</td>
</tr>
<tr>
<td>10Li10Ca80B</td>
<td>0.041</td>
<td>8.45</td>
</tr>
<tr>
<td>10Li10Sr80B</td>
<td>0.100</td>
<td>8.45</td>
</tr>
<tr>
<td>10Na10Mg80B</td>
<td>0.133</td>
<td>8.54</td>
</tr>
<tr>
<td>10Na10Ca80B</td>
<td>0.063</td>
<td>8.54</td>
</tr>
<tr>
<td>10Na10Sr80B</td>
<td>0.085</td>
<td>8.55</td>
</tr>
<tr>
<td>10K10Mg80B</td>
<td>0.244</td>
<td>8.48</td>
</tr>
<tr>
<td>10K10Ca80B</td>
<td>0.107</td>
<td>8.49</td>
</tr>
<tr>
<td>10K10Sr80B</td>
<td>0.149</td>
<td>8.51</td>
</tr>
<tr>
<td>15Na15Ca70B</td>
<td>0.013</td>
<td>9.17</td>
</tr>
<tr>
<td>20Na20Ca60B</td>
<td>0.020</td>
<td>9.41</td>
</tr>
<tr>
<td>15Li15Ca70B</td>
<td>0.008</td>
<td>9.09</td>
</tr>
<tr>
<td>20Li20Ca60B</td>
<td>0.006</td>
<td>9.48</td>
</tr>
<tr>
<td>15K15Ca70B</td>
<td>0.015</td>
<td>9.03</td>
</tr>
<tr>
<td>20K20Ca60B</td>
<td>0.030</td>
<td>9.43</td>
</tr>
</tbody>
</table>
Figure 7: Measured pH of the solution after complete dissolution of 150mg of glass in 50ml of deionized water for the glass series xR_2O-xR'O-(100-2x)B_2O_3 where x=10, 15 or 20 and R= Li, Na, or K. Solid markers indicate R'=Ca, top filled markers are R'=Mg, and bottom filled markers indicate R'=Sr. Error bars are within the symbol unless otherwise noted.

4. DISCUSSION

4.1 Solution chemistry and dissolution processes

Glass dissolution may proceed by different processes, including ion exchange, common for alkali-containing silicate glasses, and by the hydrolysis of the glass network [2]. When glasses react by an ion exchange process, a preferential leaching of certain components, such as mobile alkali ions, is evident. Ion exchange processes are often limited by the diffusion of species through the reaction layer, leading to a reduction in corrosion rate with time [2]. Reaction-limited dissolution processes, like network hydrolysis or the hydration of the bonds that link modifying cations to the glass network, are expected to
have linear time dependences. Figure 3 and Figure 4 show that the weight loss and the ion release measurements follow the linear CVM model, and Figure 2 indicates that there is not a preference for the release of one ion over another since the ion ratios are constant with time. Linear reaction kinetics and congruent dissolution have been observed previously for binary borate glasses [4, 5, 11] The linear kinetics that describe the dissolution processes of these ternary borate glasses indicate that reactions between water and the glass structure control the dissolution rates.

Two types of reactions are considered here that may control the dissolution rates of borate glasses in water. The first is the hydration of the bonds that link the modifying cations to the borate glass network. Alkali and alkaline earth cation polyhedra share oxygens with the borate polyhedra that constitute the glass network. Water will react with those bonds to hydrate the metal cations, as shown schematically here:

\[
\equiv = B-O-B^- + Na^+ + H_2O \rightarrow = B-OH + B\bar{O}_3 + Na^+ + OH^- 
\]  

(2)

The hydrated metal cations then are released into solution.

The second reaction involves the hydrolysis of the borate network, where water reacts with bridging oxygens between
neighboring borate polyhedra to form boric acid that is released into solution:

\[ \text{B-O-B} + \text{H}_2\text{O} \rightarrow \text{B-OH} + \text{HO-B} \]
\[ \text{B-OH} + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 \]

(3)

The release of the boric acid and hydrated metal ions into solution change the pH of the solution. As shown in Figure 7, glasses with greater concentrations of alkali and alkaline earth oxides, and so lower concentrations of B\(_2\)O\(_3\), increase the final pH of the solution when completely dissolved. There is less effect of the type of alkali and alkaline earth oxide, indicating that each acts as a relatively strong, dissociated base. (The concentrations of alkaline earths in these solutions exceed the solubilities of the respective alkaline earth hydroxides in deionized water [12], indicating that these ions remain dissociated under these conditions). Using the concentrations of all ions in solution, it is possible to predict the solution pH [13], and these predictions compare favorably with the measured values, as shown in Figure 7b.

There are two aspects of composition that affect the dissolution rates of the ternary alkali-alkaline earth borate glasses: the identity of the alkali and alkaline earth oxide (e.g., Figure 6) and the overall
modifier-to-borate ratio (e.g., Figure 1). These compositional effects may be understood in terms of the rate of transport of water to a reaction site \(k_{\text{trans}}\), the hydration rate of modifying cations \(k_{\text{hydration}}\) (equation 2) and the hydrolysis rate of the borate network \(k_{\text{hydrolysis}}\) (equation 3). If these three processes occur concurrently, the dissolution rate \(k_{\text{dr}}\) of a glass will then depend on the relative rates of these three processes:

\[
\frac{1}{k_{\text{dr}}} = \frac{1}{k_{\text{trans}}} + \frac{1}{k_{\text{hydration}}} + \frac{1}{k_{\text{hydrolysis}}} \quad (4)
\]

A decrease in the relative rate of any of these three processes will decrease the overall dissolution rate of the glass.

4.2 Effect of modifying cations on glass dissolution rates

As shown in Figure 6, the dissolution rates of the 10R₂O-10R′O-80B₂O₃ glasses increase in the order Li<Na<K for a constant set of alkaline earth oxides, and (in general) increase in the order Ca<Sr<Mg for a constant set of alkali oxides. For the 20R₂O-20CaO-60B₂O₃ glasses, dissolution rates also increased in the order Li<Na<K, whereas for the 15R₂O-15CaO-70B₂O₃ glasses, dissolution rates varied as Li<Na≈K (Table II).
There are at least two ways that differences in the size and charge (field strength) of the modifying cations might affect the dissolution rates of these glasses. The first involves the strength of the bonds between the modifier ions and the borate network; smaller, more highly charged cations, those with greater field strengths, form stronger, Coulombic bonds with anionic borate sites. The same trend can be seen in for the reactions and their associated equilibrium constants in Table III.

Table III: Reactions and the associated equilibrium constants at 37°C from the FactSage database.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}_2\text{O}+\text{H}_2\text{O} \rightarrow 2\text{Li}^+ + 2\text{OH}^-$</td>
<td>1.17E+17</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}+\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^-$</td>
<td>1.88E+37</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}+\text{H}_2\text{O} \rightarrow 2\text{K}^+ + 2\text{OH}^-$</td>
<td>8.30E+53</td>
</tr>
<tr>
<td>$\text{MgO}+\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$</td>
<td>1.66E-07</td>
</tr>
<tr>
<td>$\text{CaO}+\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^-$</td>
<td>1.70E+04</td>
</tr>
<tr>
<td>$\text{SrO}+\text{H}_2\text{O} \rightarrow \text{Sr}^{2+} + 2\text{OH}^-$</td>
<td>1.51E+12</td>
</tr>
</tbody>
</table>

The larger the $K_{eq}$ value the more likely each of the reactions are likely to occur.

The second way modifier field strengths may affect dissolution rates involves their influence on ion packing. Modifying ions with greater field strengths might reduce the free the volume of a borate glasses by collapsing the network around themselves. Zhang, et al.
[11] showed that alkali borate glasses densified by hydrostatic pressure have slower dissolution rates in water than glasses prepared using conventional processes. The slower reactions rates in the densified glasses were explained by a reduction in the free volume of the glass structure which reduced the access of water to bonds that could be hydrated or hydrolyzed.

In the present study, the density ($\rho$) of each glass was used to calculate the molar volume ($V_m = \frac{mw}{\rho}$, where $mw$ is the molecular weight of the glass), and molar volume was then used to calculate the packing fraction ($pf$)[14], from

$$pf = \frac{\frac{4}{3}\pi \sum r_i^3 N_i}{V_m}$$

where $r_i$ is the radius of each ion and $N_i$ is the number of each ion in the analyzed composition. The values for the ionic radii used are from Burgess, et al. [14].

Figure 8 shows that there is a correlation between packing factor and dissolution rate; those glasses with higher packing fractions generally have slower dissolution rates, consistent with the correlation noted by Zhang et al. [11] for the dissolution of densified glasses. Tighter packing of ions in the glass structure will create steric barriers to the transport of water and so reduce its access to reaction sites in
the network. This effective decrease in $k_{\text{trans}}$ would lead to a decrease in the overall glass dissolution rate (equation 4).

![Graph showing dissolution rate as a function of packing fraction for different compositions.](image)

Figure 8: The dissolution rate as a function of the packing fraction for a) the $xR_2O-x\text{CaO}-(100-2x)B_2O_3$ series, where solid symbols have Li$_2$O, top-filled have Na$_2$O and right-filled have K$_2$O and b) the $10R_2O-10R'O-80B_2O_3$ series, where solid symbols have Li$_2$O, top-filled have Na$_2$O and right-filled have K$_2$O.

4.3 Effect of boron coordination on glass dissolution rates

The correlation between modifier ion field strength and dissolution rate is general, but there are examples where the correlation fails. For example, the Mg-glasses dissolve faster than the Ca- and Sr-glasses, and this dependence cannot be explained by the relative packing fractions shown in Figure 8. There are other compositional factors that affect the dissolution rates, including the effects of B-coordination.
When a modifying oxide is added to B$_2$O$_3$, up to about 33 mole% modifying oxide, neutral boron triangles (BØ$_3$, where Ø is a bridging oxygen that links neighboring B-polyhedra) convert to anionic tetrahedral sites (BØ$_4^-$). Anionic triangles (BØ$_2$O$^-$ and BØO$_2^{2-}$) form in glasses with greater modifier contents. The relationships between composition and the fraction of tetrahedral borate sites for glasses with the general formula xR$_2$O•(1-x)B$_2$O$_3$ are given by [15]:

\[ f_{BØ_4^-} = \frac{x}{100-x}, \ 0<x<0.33 \]  
\[ f_{BØ_4^-} = \frac{300-4x}{500-5x}, \ x>0.33 \]

Velez, et al. [4] showed a minimum in the dissolution rate in water of xLi$_2$O•(1-x)B$_2$O$_3$ glasses near x=0.3, and related this to a maximum in the tetrahedral borate sites. Bunker, et al., [16] showed there was a linear relationship between the logarithm of the dissolution rates of the Li-borate glasses studied by Velez, et al., and the fraction of tetrahedral sites in the glass, and used this relationship to explain the enhanced corrosion resistance of Na-borosilicate glasses with tetrahedral sites in the network. More recently, Zapol et al. [17] used first principle calculations to explain the enhanced reactivity of B[3]-O
bonds compared to B[4]-O bonds. Zapol, et al., [17] also noted that protonating the bridging oxygen to a tetrahedral borate, by exchanging, for example, the proton for an alkali ion, destabilized that bond, causing it to hydrolyze. This is the proton-catalyzed hydrolysis reaction noted by Bunker, et al., and is the reason that borosilicate (and borate) glasses do not selectively leach alkalis without the concomitant hydrolysis and release of borate species, except under very acidic conditions [16].

The structure of the glasses in this study have been characterized by solid state nuclear magnetic resonance spectroscopy [9], which provides a measure of the compositional dependence of fBØ4-. Those results are summarized in Table 1. And are used in Figure 9a which compares the effects of total modifier content (R₂O+CaO) on the boron-release rates and the fractions of tetrahedral borate sites for the glasses in the xR₂O-xCaO-(1-2x) B₂O₃ glasses. The dissolution rates go through minima near 30 mole% modifying oxide, the same compositional range where the fraction of borate sites is maximized. Figure 9b shows the relationship between B-release rates (log scale) and the fraction of tetrahedral borate sites for all glasses analyzed. There is a clear trend that is consistent with Bunker’s observation [16]: increasing the fraction of tetrahedral borate sites in these ternary glasses reduces their dissolution rates.
Figure 9: Dissolution rates based on boron release for a) $xR_2O-xCaO-(100-2x)B_2O_3$ glass series plotted with the $fB\theta_4^-$ for the $Na_2O-CaO-B_2O_3$ glasses (open boxes) (the $x=5$ mole% data was added for clarity) and b) the dissolution rate for all glasses plotted with the $fB\theta_4^-$. Dashed lines are guides for the eye.

These results help explain the effect of the identity of the alkaline earth oxide on the dissolution rates of the $10Na_2O-10R'O-80B_2O_3$ glasses (Figure 6). Despite the greater field strength of $Mg^{2+}$,
the Na-Mg-glass has a greater dissolution rate than both the Na-Ca- and Na-Sr- glasses. The Mg-glass, however, also has a lower value of fBØ4− (0.25) than the Ca- and Sr-glasses (0.30). The lower value of fBØ4− for the Mg-glass results from the disproportionation of the tetrahedral sites into more reactive anionic trigonal sites in the borate melts [14]. Thus, the increase in \( k_{\text{hydrolysis}} \) due to the reduction of BØ4− offsets any decrease in \( k_{\text{hydration}} \) because of greater field strength, and so the \( k_{\text{dr}} \) of the Mg-glass is greater. Similar reasoning applies to some of the other compositional trends. For example, faster hydration \( (k_{\text{hydration}}) \) in the order K>Na>Li increases the \( k_{\text{dr}} \) in the same order of alkalis in the respective 10R2O-10CaO-80B2O3 and 20R2O-20CaO-60B2O3 series (Figure 9a). The alkali identity dependence of \( k_{\text{dr}} \) for the 15R2O-15CaO-70B2O3 series, however, is much less because of the competing effects of lower \( k_{\text{hydrolysis}} \) associated with the maximum BØ4− contents.

5. CONCLUSIONS

Particles of ternary alkali-alkaline earth borate glasses congruently dissolve in water, releasing all ions simultaneously, and the dissolution rates are well described by a contracting volume model that indicates a reaction controlled mechanism for dissolution. The
dissolution rates depend both on the identities of the alkali and alkali earth oxides and on their relative concentrations. In general, dissolution rates increase in the order Li<Na<K and Ca<Sr<Mg, and minima in dissolution rates occur around 30 mole % for the total alkali and alkaline earth oxide content.

The compositional dependence of the dissolution rates have been described by the relative rates of two reactions: the hydration of the modifier polyhedra and the hydrolysis of the borate network. The transport of water to reaction sites in the glass network was also considered. Low field strength cations hydrate more quickly and so contribute to faster dissolution rates, whereas compositions with greater fractions of tetrahedral borate species hydrolyze more slowly, contributing to slower dissolution rates. Glasses that have lower free volumes also dissolve more slowly, indicating that steric hindrances to water may affect the relative hydration and hydrolysis rates.

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REFERENCES


IV. COMPOSITIONAL DESIGN OF BORATE-BASED BIOACTIVE GLASSES

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ABSTRACT

Many first generation borate bioactive compositions were created simply by replacing the silica with $\text{B}_2\text{O}_3$ in well-known silicate compositions. In the present work, a seven component ($\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{MgO}$, $\text{CaO}$, $\text{B}_2\text{O}_3$, $\text{SiO}_2$, and $\text{P}_2\text{O}_5$) mixture model design was used to predict composition-property relationships to optimize the properties of new borate-based bioactive compositions for specific applications. Melt viscosity, thermal expansion coefficient, liquidus temperature and crystallization tendency were determined, as were dissolution rates in simulated body fluid (SBF). The addition of silica suppresses crystallization tendency and increases viscosity, whereas the addition of $\text{P}_2\text{O}_5$ has an opposite effect on the crystallization tendency. When

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immersed in SBF at 37°C, the glasses convert to hydroxyapatite (HA) with a wide range of reaction rates that are dependent on the silica content.

**Keywords:** Design of Experiment (DOE), Borate glass, Borosilicate glass, bioactive glass, Ti 6Al-4V, Dissolution Rate, Hydroxyapatite

1. **INTRODUCTION**

Silicate glasses have been used for biomedical applications since Hench first developed Bioglass (45S5) in the 1960’s [1]. 45S5 is a Na$_2$O-CaO-SiO$_2$ glass modified by P$_2$O$_5$ and has been found to bond to bone and to soft tissue. 45S5 has a tendency to crystallize during sintering and compositions like 13-93 glass were developed for biomedical applications where thermal stability was desired [2].

Borate glasses such as DermaFuse, produced by Mo-Sci Corporation, have recently been developed for biomedical applications [3, 4]. In the presence of phosphate-containing solutions, including simulated body fluid (SBF) and under *in vivo* conditions, calcium-containing borate glasses convert to hydroxyapatite (HAp) more quickly than do silicate bioactive glasses [5]. Borate glasses are also good hosts for ions that can promote healing of soft and hard tissue.
One borate glass composition that has received significant attention is designated 1393-B3 (B3) and is based on 13-93, the thermally-stable silicate bioactive glass, for which the SiO$_2$ compositional component has been replaced with B$_2$O$_3$, based on weight percent [7].

In order to design a bioactive glass composition, many factors need to be considered. Vedel, et al. [8], used a compositional design approach to optimize the properties of silicate-based bioactive glasses, and a similar design approach is used in the present study for borate glasses. The compositional dependences of melt viscosity [9] and crystallization characteristics [10], thermal expansion coefficient, and reactivity in simulated body fluid [11] have been determined and are used to design borate-glass compositions for biomedical applications.

2. EXPERIMENTAL PROCEDURE

A seven component mixture model design was made using Design Expert 8 (Stat-Ease, Inc., Minneapolis, MN). A total of 38 runs were used, 28 model points with five replicates and five compositions to estimate lack of fit. The mixture experiment was designed using the compositional parameters shown in Table I.
Table I: Compositional parameters for developing the seven-component mixture design.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Minimum (mole%)</th>
<th>Maximum (mole%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>45</td>
<td>70</td>
<td>Want to minimize effect of boron coordination change</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>0</td>
<td>20</td>
<td>Use to control dissolution rate and melt behavior</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>0</td>
<td>20</td>
<td>Use to control dissolution rate and melt behavior</td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
<td>20</td>
<td>Use to control crystallization tendency and melt behavior</td>
</tr>
<tr>
<td>CaO</td>
<td>15</td>
<td>40</td>
<td>Want CaO available to form hydroxyapatite</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>0</td>
<td>5</td>
<td>Use to aid formation of hydroxyapatite About maximum allowable in B3-like composition</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>0</td>
<td>20</td>
<td>Use to adjust viscosity</td>
</tr>
</tbody>
</table>

Compositions were batched using reagent grade raw materials to produce 100 grams of glass. Batches were melted in a platinum-rhodium crucible in air at 850-1300°C and 30-60 minutes, depending on the compositions. Melts were poured or quenched between copper plates, depending on the composition. Each run was characterized by x-ray diffraction (XRD) using a PANalytical X’Pert Pro Multi-purpose diffractometer with PiXcel detector to detect crystallinity. Non-crystalline samples that were also not transparent were considered to be phase-separated. Some melts were only glassy if they were quenched between copper plates (referred to as quenchable). As-prepared compositions were determined by dissolving glass particles in
1% nitric acid and measuring the ion concentrations with inductively
coupled plasma-optical emission spectroscopy (ICP-OES), Perkin Elmer
Optima 2000 DV. These measured compositions were used in analysis
of the design rather than the nominal compositions.

Glass cylinders 5mm in diameter and 5-6mm tall were core-
drilled from annealed samples, polished, and then used for the thermal
expansion and parallel plate viscosity (PPV) measurements (Perkin
Elmer 7-e dynamic mechanical analyzer). The coefficient of thermal
expansion (CTE) was measured between 100 and 400°C at a heating
rate of 10°C/minute. A static force of 500mN was applied to each
cylinder which was then heated at 2 °C/minute above the glass
transition temperature, and the viscosity was determined from the
cylinder compression rate, following the method described by Rincon
and Romero [12].

High temperature viscosity measurements were done using a
Brookfield DV-II viscometer with a platinum-rhodium spindle and
crucible. The viscometer was calibrated using standard viscosity oils
from 0.1-12.5 Pa·s. Each glass was heated to above its liquidus
temperature in a SiC element furnace. The temperature was then
decreased in 25°C increments, held for three minutes, and then
viscosity was measured at different spindle rotational speeds, from 0.3
to 60 RPM.
The PPV and rotational viscosity data were fit using the MYEGA equation [13]:

$$\log_{10} \eta(T) = \log_{10} \eta_\infty + (12 - \log_{10} \eta_\infty) \frac{T_g}{T} \exp \left[ \left( \frac{m}{(12-\log_{10} \eta_\infty) - 1} \right) \left( \frac{T_g}{T} - 1 \right) \right]$$  \hspace{1cm} (Eq. 1)

where $m$ is the fragility of the super-cooled liquid, $T_g$ is the glass transition temperature (K), $\eta$ is the viscosity of the melt (Pa·s) and $\eta_\infty$ is the viscosity of the melt at infinite temperature. For fitting the PPV and rotational viscosity data, these parameters were restricted to $-6 < \log_{10} \eta_\infty < 0$, $T_g = \text{measured } T_g \pm 20K$, and $m > 0$.

Differential thermal analysis (DTA) was done using a Perkin-Elmer DTA 7 on powders (75-150 µm). Characteristic temperatures, such as the glass transition temperature ($T_g$), based on the inflection point of the curve, the onset of crystallization ($T_x$), and the onset of melting ($T_m$), were determined for each glass-forming composition at a heating rate of 10 °C/minute. Heating rates of 5, 10, 20 and 30 °C/minute were used to determine the liquidus temperature, using the end of the melting peak ($T_{m,\text{end}}$), following Ferreira’s method [14].

The viscosity at the liquidus temperature was determined, as was the slope of the viscosity curve at the liquidus temperature. The latter was calculated from the derivative of the MYEGA equation with respect to $T_g/T$ at the liquidus temperature.
Chemical reactivity was determined using thirty milligrams of powder (75-150 µm) that was washed with ethanol to remove fines and then added to a polypropylene vial (in triplicate) with 50 ml of simulated body fluid [15] that were then were placed in a 37°C oven. Aliquots of 150 µL were taken from the vials after various times, up to 14 days, and diluted 1:100 in 1% nitric acid for ICP-OES analysis of boron, silicon, calcium and phosphorus ion concentrations. The boron ion concentration data were then fit using the three-dimensional diffusion [16, 17] (3D) (Eq. 2) model to determine the reaction rate (k).

\[ k_t = \left[ 1 - (1 - \alpha)^\frac{1}{3} \right]^2 \]  
(Eq. 2)

where \( t \) is time and \( \alpha \) is the concentration of boron in solution divided by the total amount of boron in the glass. After four weeks on test, the reacted particles were analyzed using XRD and Raman spectroscopy (labRAM Aramis Horiba Jobin Yvon with 785 diode laser). Some particles were mounted in poly (methyl methacrylate) (PMMA) and polished to obtain cross-sections. These samples were then analyzed using scanning electron microscopy (SEM) (Hitachi S-4700 FESEM) with energy dispersive spectroscopy (EDS) to characterize the microstructures and chemical compositions of the reacted particles.
The response variables that were measured for this study were $T_g$, CTE, the viscosity at the liquidus temperature ($\eta$ at $T_{liq}$), the change in viscosity at the liquidus temperature (slope at $T_{liq}$) ($\partial[\log \eta/(T_g/T)]$ from the MYEGA equation), and the reaction rate constant ($k$) in SBF based on the 3D kinetic model. Analysis of the response variables was done using SAS 9.0 (SAS Institute Inc., Cary, NC) and Design Expert 8 (Stat-Ease, Inc., Minneapolis, MN). A stepwise regression analysis was done including three-way interactions, squared terms, two-way interactions and main effects, with an $alpha in$ and an $alpha out$ equal to 0.1.

3. RESULTS AND DISCUSSION

3.1 Glass forming range

Only 19 of the initial 38 runs in the design formed crystal-free, transparent glasses and so the model was refined by a partition method using JMP Pro 10.0 software (SAS Institute Inc., Cary, NC), and a screening method, using Design Expert 8. The partition method was used to determine the approximate compositional limits for the glass forming regions in the seven-component system, and these results are summarized in Figure 1. Figure 1 that there was about a 70% chance to form a glass from compositions with less than 3.4 mol% P$_2$O$_5$. For glasses with less than
3.4 mol% P₂O₅, there was nearly an 80% chance of forming a glass if the composition contained less than 11.9 mol% K₂O. If the composition also has less than 11.8 mol% MgO, there was better than a 90% chance that it will form a glass.

The screening method for determining the glass-forming range relies on a classification of glass-forming tendency for the 38 runs completed. The classification parameter used is 1=glass, 2=quenched glass, 3=phase separated, and 4=crystallized. Figure 2 shows an example of the output of the screening analysis for the CaO-MgO-P₂O₅ sub-system. Increasing the P₂O₅ increases the value of the classification parameter, indicating a lower tendency for homogeneous glass formation.

Figure 1: Summary of the partition method analysis of the compositional factors that determine glass formation.
Each of the coefficients are considered statistically with p-values less than 0.05 and each model have high (>4) signal to noise ratios indicating that the model can be used for this design space. The $R^2$ value is an indication on how well the model fits the measured data. However, it can be artificially inflated by over-fitting. The adjusted $R^2$ value avoids this by only increasing if the added term increases the $R^2$ value more than expected due to chance. The predicted $R^2$ value will indicate if the model only fits the data that has been measured or if the added term increases the ability of the model to predict future measurements. This means that the $R^2$ value will always be higher...
than the adjusted $R^2$ value and the predicted $R^2$ value but the closer they are to each other the better the model will be. This means that the model for the glass forming screening parameter and $k$ will not be able to predict values as well as the models can predict the other response variables.

### 3.2 Composition-property model development

A stepwise regression method was used instead of quadratic analysis for the model of the compositional dependence of glass properties. The constant coefficients that resulted from these analyses are shown in Table II.

Table II: Coefficients for the composition-property model based on stepwise analysis in Design Expert 8 where components are in mole%. All coefficients in the table have a significance level of 0.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>glass forming</th>
<th>$T_g$ (°C)</th>
<th>CTE ($\times 10^{-7}$/°C)</th>
<th>$k$ (hr$^{-1}$)</th>
<th>log $\eta$ at $T_{liq}$ (Pa·s)</th>
<th>slope at $T_{liq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_2O_3$</td>
<td>6.04E-03</td>
<td>4.80E+00</td>
<td>4.28E-01</td>
<td>1.23E-04</td>
<td>2.03E-02</td>
<td>2.13E-01</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-2.12E-01</td>
<td>-1.22E+00</td>
<td>7.11E+00</td>
<td>-9.93E-05</td>
<td>-4.18E-02</td>
<td>-1.54E-01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>5.03E-01</td>
<td>5.02E-01</td>
<td>3.60E+00</td>
<td>7.39E-04</td>
<td>-1.19E-01</td>
<td>2.13E-02</td>
</tr>
<tr>
<td>MgO</td>
<td>9.53E-02</td>
<td>6.46E+00</td>
<td>2.20E+00</td>
<td>-6.87E-04</td>
<td>3.47E-03</td>
<td>-8.25E-01</td>
</tr>
<tr>
<td>CaO</td>
<td>1.23E-02</td>
<td>2.03E+00</td>
<td>1.29E+00</td>
<td>2.36E-04</td>
<td>-3.12E-02</td>
<td>1.53E-01</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>-2.44E+00</td>
<td>1.04E+01</td>
<td>-7.82E-01</td>
<td>-7.54E-04</td>
<td>1.22E-01</td>
<td>3.25E-01</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>8.41E-02</td>
<td>8.29E+00</td>
<td>-6.65E-01</td>
<td>-2.59E-05</td>
<td>-1.10E-01</td>
<td>4.73E-01</td>
</tr>
<tr>
<td>$B_2O_3$*$Na_2$O</td>
<td></td>
<td></td>
<td>-6.76E-02</td>
<td></td>
<td></td>
<td>4.31E-03</td>
</tr>
<tr>
<td>$B_2O_3$*$K_2$O</td>
<td></td>
<td></td>
<td>-6.87E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_2O_3$*$MgO$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.33E-02</td>
<td></td>
</tr>
<tr>
<td>$B_2O_3$*$CaO$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.26E-01</td>
<td></td>
</tr>
<tr>
<td>$B_2O_3$*$P_2$O$_5$</td>
<td></td>
<td></td>
<td>3.73E-02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O*$CaO$</td>
<td></td>
<td></td>
<td>1.03E-02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O*$SiO_2$</td>
<td></td>
<td></td>
<td>4.31E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II: Coefficients for the composition-property model based on stepwise analysis in Design Expert 8 where components are in mole%. All coefficients in the table have a significance level of 0.1.  

<table>
<thead>
<tr>
<th>glass forming</th>
<th>( T_g ) (°C)</th>
<th>CTE (x10^{-7}/°C)</th>
<th>( k ) (hr^{-1})</th>
<th>log ( \eta ) at ( T_{liq} ) (Pa·s)</th>
<th>slope at ( T_{liq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)O*Na(_2)O</td>
<td>1.33E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO*MgO</td>
<td></td>
<td>-5.20E-02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(_2)O(_5)*P(_2)O(_5)</td>
<td>1.54E-01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO(_2)*SiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(_2)O(_3)<em>Na(_2)O</em>CaO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(_2)O(_3)<em>Na(_2)O</em>P(_2)O(_5)</td>
<td>5.34E-06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(_2)O(_3)<em>Na(_2)O</em>SiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(_2)O(_3)<em>K(_2)O</em>MgO</td>
<td>-3.91E-04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)O<em>K(_2)O</em>MgO</td>
<td>-3.06E-02</td>
<td>6.14E-05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)O<em>K(_2)O</em>P(_2)O(_5)</td>
<td>-2.13E-04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)O<em>K(_2)O</em>SiO(_2)</td>
<td>-1.77E-03</td>
<td>1.95E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)O<em>MgO</em>SiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(_2)O<em>CaO</em>SiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.22E-03</td>
</tr>
<tr>
<td>K(_2)O*P(_2)O(_5)*SiO(_2)</td>
<td>-1.47E-02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO<em>CaO</em>P(_2)O(_5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.07E-03</td>
</tr>
<tr>
<td>CaO*P(_2)O(_5)*SiO(_2)</td>
<td>2.27E-02</td>
<td>-9.12E-06</td>
<td>7.70E-04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R\(^2\) value 0.899 0.994 0.991 0.973 0.992 0.999  
Adj R\(^2\) value 0.845 0.989 0.982 0.940 0.982 0.998  
Predi\(^2\) value 0.715 0.978 0.974 0.824 0.893 0.995

A predicted property is calculated from the sum of the products of each coefficient and the related composition (mole%), including the cross-product terms. For example, an examination of the coefficients for \( T_g \) and CTE in Table II reveals that increasing the Na\(_2\)O-content of a glass decreases the former and increases the latter, whereas increasing the silica content has an opposite effect.
The compositional design model was first tested by comparing the properties of the B3 composition predicted from the model and compared with measured values. Then the model was used to develop a glass composition with specific properties to be used as a coating for Ti-6Al-4V implants which widely used in orthopedic applications. The predicted and measured properties for B3 are shown in Table III, as well as the confidence intervals (95%). Some of the parameter models are better than others. That could be due to larger error (less confidence) in experimental measurements, in other words less accurate measurements lead to less accurate predictions such as viscosity and dissolution rate measurements. One way to decrease the error associated with a prediction is to do another iteration of the experiment or have greater accuracy in the property measurements for the runs in the design.

<table>
<thead>
<tr>
<th>Response</th>
<th>Measured</th>
<th>Predicted (95% confidence interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Formation</td>
<td>1</td>
<td>1±0.4</td>
</tr>
<tr>
<td>T_g (°C)</td>
<td>508±3</td>
<td>507.2±6.8</td>
</tr>
<tr>
<td>CTE (×10⁻⁷) (°C⁻¹)</td>
<td>116±5</td>
<td>120±2.9</td>
</tr>
<tr>
<td>k (hrs⁻¹)</td>
<td>0.006±0.001</td>
<td>0.008±0.0023</td>
</tr>
<tr>
<td>η at T_liquid (Pa.s)</td>
<td>-0.45±0.1</td>
<td>-0.73±0.1</td>
</tr>
<tr>
<td>Δη/ΔT (Pa.S/°C)</td>
<td>12.0±0.1</td>
<td>18.4±0.1</td>
</tr>
</tbody>
</table>
3.2.1 Melt Properties

The viscosity of a glass melt determines how that melt can be processed. Melts with greater viscosity at the liquidus temperature form glass more easily on cooling [18] and can be more readily processed into fibers. Melts that do not have a high viscosity but do exhibit rapid increases in viscosity on cooling through the liquidus temperature also have an increased chance of glass formation. Figure 3 shows the viscosity curves for two glasses from the study, glass 18 with a high log viscosity (0.96 Pa s) and greater slope (23.4) at the liquidus temperature and the glass 23 with low log viscosity (-1.18 Pa s) and lower slope (16.8) (glass 23) at the liquidus temperature. The differences in the kinetic glass forming parameters indicate that glass 18 should more readily form glass compared to glass 23. The compositions for these glasses are shown in the inset for Figure 3. Based on the results from the partition method, glass 23 is an exception in terms of glass forming. Glass 23 has a high amount of P₂O₅, MgO and K₂O, all of which were found to decrease the likelihood of forming a glass.
The DTA analyses of two compositions, glass 17 and glass 18, did not reveal an exothermic peak for crystallization at the heating rates tested in this study (5-30°C/min) (Figure 4). Also shown in Figure 4 is the DTA scan of B3, which has a distinct crystallization peak. These results indicate that glasses 17 and 18 have greater stability against crystallization than B3. Glasses 17 and 18 also have greater liquidus temperature viscosities and greater changes in the viscosity at the liquidus temperature than B3, consistent with better kinetic glass forming ability parameters (Table IV).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Glass 18</th>
<th>Glass 23</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂O₃</td>
<td>63.0</td>
<td>46.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CaO</td>
<td>13.4</td>
<td>14.7</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>8.6</td>
<td>0.0</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.0</td>
<td>19.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.0</td>
<td>14.7</td>
</tr>
</tbody>
</table>
Table IV: $T_g$, viscosity at $T_{liq}$ and slope at $T_{liq}$ values predicted for the glasses shown in Figure 4.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$\eta T_{liq}$ (Pa·s)</th>
<th>slope at $T_{liq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3</td>
<td>507</td>
<td>-0.73</td>
<td>18.4</td>
</tr>
<tr>
<td>17</td>
<td>508</td>
<td>1.39</td>
<td>20.5</td>
</tr>
<tr>
<td>18</td>
<td>559</td>
<td>1.09</td>
<td>23.6</td>
</tr>
</tbody>
</table>

3.2.2 Reaction in Simulated Body Fluid

Conventional bioactive glasses react in the body to convert to a hydroxyapatite (HAp)-like material, which is deposited on the surface...
of the reacting glass. This HAp-like phase is considered to be an indication of bioactivity for biomaterials since it will readily interact with bone[19]. Different applications need different responses from the glass. Glass response in the body includes the release of ionic constituents and conversion to a new biocompatible material. Thus studying the rate of this phenomenon is particularly important for the design of new bio-glass compositions.

The reaction rate for these glasses was calculated from the release of boron into simulated body fluid (SBF) and examples of these tests are shown in Figure 5 where the percent of glass reacted is plotted against reaction time for four compositions, using Eq.2. The slope of the linear fit is the reaction rate (k in Eq. 2). The glasses in this study reacted completely within three days in SBF and the reaction rate constants varied by an order of magnitude from 2.4e-3 to 28.6e-3 hours⁻¹.
Figure 5: Range of reaction rate constants for glasses in SBF, determined from the 3D diffusion kinetic model (Eq. 2).

Figure 6 shows the XRD pattern for glass 17 reacted in SBF for four weeks at 37°C. This pattern indicates a phase that is similar to hydroxyapatite. Similar results were obtained for all of the borate glasses exposed to SBF for four weeks.
Figure 6: Analysis of the reaction product of the run 17 glass in SBF for 4 weeks using XRD. Stick pattern is HAp JCPDS reference 00-001-1008.

The microstructures and compositions of reacted particles (four weeks in SBF at 37°C) of glasses 16 and 17 and B3 are shown in Figure 7. The onion-like microstructure (layer by layer) was observed for all three glasses; however the reacted layers were thicker and have greater Ca/P ratios for the B3 and glass 16 particles than the glass 17 particles. These differences be attributed to the greater CaO-contents of B3 (23.9 mol%) and glass 16 (23.3 mol%), compared to glass 17 (15.0 mol%). It has been shown that greater calcium contents result in thicker HAp layers with greater Ca/P ratios when borate glasses react in phosphate-containing solutions [6].
Figure 7: SEM images and EDS maps of the reaction products formed after the exposure of particles of three different glasses B3, glass 16 and glass 17 to SBF for 4 weeks at 37°C.

3.3 Using the compositional design model

The compositional design model was used to formulate glasses for coating Ti 6Al-4V. Titanium 6Al-4V is an alloy that has been used for orthopedic or dental implants [20, 21]. Bioactive glass coatings that convert to HAp and create a strong bond to bone have been proposed for titanium [22-25]. Typical processing would entail heating the titanium alloy into a temperature range where the glass will soften and adhere to the titanium alloy. As the sample cools, a mismatch in
the coefficient of thermal expansion (CTE) could cause the coating to break.

The design criteria for a new borate-based coating material include a minimized glass forming parameter, a low $T_g$, to minimize the sealing temperature, and the CTE of the glass should be close to that of the Ti 6Al-4V, approximately $95 \times 10^{-7} / \degree C$. Two designs were considered based on different weighting systems: one that emphasized the CTE match and one that emphasized the glass forming parameter. The compositions of these glasses along with their predicted and measured $T_g$ and CTE are presented in Table V.

Table V: Compositions of glasses, in mole %, that were predicted to have a CTE similar to that of Ti 6Al-4V with the predicted and measured properties.

<table>
<thead>
<tr>
<th>Mol%</th>
<th>Ti-1</th>
<th>Ti-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_2$O$_3$</td>
<td>46.5</td>
<td>69.8</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>2.6</td>
<td>8.6</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>6.4</td>
<td>5.3</td>
</tr>
<tr>
<td>MgO</td>
<td>13.2</td>
<td>0.0</td>
</tr>
<tr>
<td>CaO</td>
<td>15.8</td>
<td>15</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>2.9</td>
<td>1.3</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>12.6</td>
<td>0.0</td>
</tr>
<tr>
<td>$T_g$ ($\degree C$)</td>
<td>544/548</td>
<td>499/490</td>
</tr>
<tr>
<td>CTE ($10^{-7}$) ($\degree C^{-1}$)</td>
<td>95/89</td>
<td>95/97</td>
</tr>
</tbody>
</table>
The measured CTE and $T_g$ values for these glasses are in agreement with predicted values using the statistical analysis of the 7-component model in this study.

4. CONCLUSION

Design of experiment principles were used to design new bioactive borate glasses and to analyze the composition-property relationships in a seven-component system. Although only half of the runs formed glass, using a stepwise analysis it was possible to determine the relationships between glass composition and properties (thermal, chemical, etc.). Using a coded method it was shown that the glass forming ranges could be predicted, increasing the chance of glass formation for all runs in next designs. The validity of the model was evaluated by predicting different properties of well-known borate glasses, like B3. Also, it was shown that model could be used to design new glasses with certain properties for specific applications. New glasses designed to have minimized $T_g$ at the same time match the CTE of Ti 6Al-4V alloy to be used potentially as coatings for orthopedic implants. The results for the two glasses that were tested were in agreement with the predictions of the model, which makes this model a tool for new bioactive glass design for
different applications. Further validation of the model is needed however, to strengthen the predictive ability.

ACKNOWLEDGMENTS

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REFERENCES


SECTION

3. SUMMARY AND AFTERWORDS

The following is a summary of the conclusions drawn from the research completed for this dissertation. Additionally, recommendations for future experiments are provided.

1) The glass forming ability and the glass stability of glasses in the Na\textsubscript{2}O-CaO-B\textsubscript{2}O\textsubscript{3} system were determined and linked to the processing ability of these glass compositions. It was determined that glasses in this system are unlikely to be able to be held in the viscosity range that is typically used for fiber drawing without crystallizing. This indicates that a more complex composition is needed to avoid crystallization on drawing. It was also found that glasses in this system are not likely to crystallize if they are held in the viscosity range typical of sintering. These glasses should sinter at a lower temperature than the onset of crystallization. The primary glass stability parameter, the Hruby parameter, was shown to be dependent on the sample tested when the parameters from this study were compared to those measured in other
studies. This is why the Hruby parameter was not used as an indication of glass forming ability.

Overall, the most promising compositional range for glasses that fit the desired processing parameters have less than 70 mole% B$_2$O$_3$ and CaO contents greater than 15 mole%. This range balances the glass forming ability and the glass stability of the compositions and provided a starting place for further study that was done for the paper “Compositional design of borate-based bioactive glasses.”

2) The structure of ternary alkali-alkaline earth-borate glasses was studied using NMR and Raman spectroscopy. NMR analysis indicated that the identity of the alkali oxide in the glass did not change the fBØ$_4^-$ but that the presence of MgO, instead of either CaO or SrO caused a significant decrease in the fBØ$_4^-$. This was attributed to disproportionation of the superstructural units to form more boroxol rings and NBO instead of four-coordinated boron units in the glass structure due to the high field strength of the Mg$^{2+}$ relative to the other modifiers. This was supported by Raman spectroscopy that indicated increased boroxol rings in place of triborate rings. The Raman also indicated that there was a slight change in the fBØ$_4^-$ with the changing alkali oxide present in the glass,
based on the relative intensities of the peaks associated with boroxol and triborate rings; this increased with increasing ion size, Li<Na<K. The structure of these glasses provides a basis for analyzing the dissolution behavior of simple alkali-alkaline earth borate glasses that were studied in the paper “Dissolution of ternary alkali-alkaline earth-borate glasses in water.”

3) The ternary alkali-alkaline earth-borate glasses were found to dissolve congruently through a reaction controlled mechanism, following the contracting volume model for spherical particles. The dissolution rates of the glass powder in DI water were linked to the structure. Glasses with increasing B$_2$O$_3$ concentrations, and thus higher fBØ$_4^-$, had slower reaction rates in water. An increase in the B$_2$O$_3$ content of the glass was also found to control the pH of the solution after dissolution. The identity of the alkali or alkaline earth present in the glass did not affect the pH of the solution. In glasses with similar fBØ$_4^-$ the field strength of the modifying ion controlled the reaction rate. The higher the field strength the slower the glass dissolution. It is proposed that this change in the overall reaction rate is due to a change in the relative rates of hydration and hydrolysis.
4) A mixture design was used to determine the effects of different components on the glass forming (including a screening parameter, the viscosity at the liquidus temperature and the change in the viscosity at the liquidus temperature), thermal expansion coefficient, glass transition temperature, and dissolution rate in SBF. These parameters allow glass compositions to be developed for applications with different requirements. There was evidence of interactions between the components but, generally, it was found that an increase in SiO$_2$ caused an increase in the viscosity at the liquidus temperature and that the addition of alkali such as potassium increased the dissolution rate. Overall, the model allowed for the prediction of some properties of the glass but further verification of the design is needed.

This dissertation provides a starting place for compositional design of borate bioactive glasses; however, there is more that can be done.

1) The role of the alkali and alkaline earth ions in the structure of borate glasses can be further investigated, particularly as it pertains to the dissolution rate of borate glasses. Determining
whether the field strength of the modifying ions is affecting the hydration of the network through steric concerns or through changing the relative rates for hydration vs hydrolysis would be useful to determine.

Determining the effect of the free volume on the role of water diffusion into the glass structure can be further studied by making a series of glasses of the same composition but that have changing free volume by controlling the cooling rate of the melt. If there is a difference seen in the dissolution rate of a series with changing free volume this could provide further information about the role of water diffusion into the glass structure on the dissolution rate of the glass.

It might not be possible to get a large enough change in the free volume of the glass through this method. The use of pressure to compress the structure, similar to Zhang’s study would allow for further study, however the compression of the structure could lead to strained bonds that would preferentially react so it is preferred to use cooling rate to control the structural differences.

The effect of the field strength of the ions on the dissolution of the borate glasses can be further studied by looking at the effect of changing the ratio between two
modifiers while keeping the amount of $\text{B}_2\text{O}_3$ in the composition constant.

To further look at the effect of the MgO on the dissolution rate of the glass it is important to look at changing the overall content. Since the dissolution rate is dependent on the structure of glass if it is possible to get a similar $\text{fBO}_4^-$ then the MgO containing glass should react slower based on the field strength.

2) More validation of the model developed in “Compositional design of borate-based bioactive glasses” needs to be done. This should include testing compositions of interest for specific applications. Glasses should be developed with extremes for the predicted dissolution rate in SBF as this is a parameter of particular interest. Further iterations of the glass compositional design could also be done in order to refine the predictive capabilities of the empirical model. Future designs could build off what was determined to affect the glass forming region, such as limiting the $\text{P}_2\text{O}_5$ content to below 3.4 mole %, in order to have more compositions successfully form glasses. This could lead to narrower prediction intervals and increase the efficacy of the model.
Additionally, it might be possible to expand the design to include glasses with lower amounts of B$_2$O$_3$. Recommended compositional ranges for the next iteration can be seen in the following table.

**Table 3-1: Recommended compositional ranges for the next iteration for design of a borate-based bioactive glass.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Minimum content (mole%)</th>
<th>Maximum content (mole%)</th>
</tr>
</thead>
<tbody>
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<td>70</td>
</tr>
<tr>
<td>Na$_2$O</td>
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<td>15</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
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</tr>
<tr>
<td>CaO</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

Other response variables could also be added to the design. Parameters such as the thickness of the reaction layer that forms during reaction in SBF could be useful to be able to optimize for certain applications. For example would healing applications may not need a thick layer of HAP while a glass composition that would form hollow tubes to direct blood vessel growth might benefit from having a thicker reaction layer that could provide some protection.

Another parameter that may be of interest is the pH of the SBF as the glass reacts. The release of alkali ions at the
site of implants can cause a negative reaction in the healing of the tissue, possibly due to the pH of the solution. If this change in the pH can be controlled then the negative effect seen could be minimized.
APPENDIX A

SUPPLEMENTAL INFORMATION FOR VISCOSITY, CRYSTALLIZATION AND GLASS-FORMING TENDENCY OF Na$_2$O-CaO-B$_2$O$_3$ MELTS
Figure A1-1: Viscosity curves for the xNa$_2$O-(10-x)CaO-90B$_2$O$_3$ glass series where x = 5 and 10 mole %.
Figure A1-2: Viscosity curves for the $x\text{Na}_2\text{O}-(20-x)\text{CaO}-80\text{B}_2\text{O}_3$ glass series where $x=5$, 10 and 15 mole %.
Figure A1-3: Viscosity curves for the xNa$_2$O-(30-x)CaO-70B$_2$O$_3$ glass series where x=7.5, 15 and 22.5 and 30 mole %.
Figure A1-4: Viscosity curves for the $x\text{Na}_2\text{O}-(35-x)\text{CaO}-65\text{B}_2\text{O}_3$ glass series where $x=0, 7.5, 15, 20, 27.5$ and $35$ mole %.
Figure A1-5: Viscosity curves for the $x\text{Na}_2\text{O}-(40-x)\text{CaO}-60\text{B}_2\text{O}_3$ glass series where $x=5$, 10, 15, 20 and 30 mole %.
APPENDIX B

SPECTROSCOPIC STUDY OF THE STRUCTURE OF Na$_2$O-CaO-B$_2$O$_3$
SYSTEM
Figure B-1: Raman spectra, measured with a 488nm laser, for the $x\text{Na}_2\text{O}-(100-x)\text{B}_2\text{O}_3$ series where $x=10$, 30 and 35 mole %.
Figure B-2: Raman spectra, measured with a 488nm laser, for the xNa$_2$O-(20-x)CaO-80B$_2$O$_3$ series, where x=5, 10 and 15 mole %.
Figure B-3: Raman spectra, measured with a 488nm laser, for the $x\text{Na}_2\text{O}-(30-x)\text{CaO}-70\text{B}_2\text{O}_3$ series, where $x=7.5$, 15, 22.5 and 30 mole %.
Figure B-4: Raman spectra, measured with a 488nm laser, for the $x\text{Na}_2\text{O}-(35-x)\text{CaO}-65\text{B}_2\text{O}_3$ series, where $x=0, 7.5, 15, 20, 27.5$ and 35 mole %.
Figure B-5: Raman spectra, measured with a 488nm laser, for the xNa$_2$O-(40-x)CaO-60B$_2$O$_3$ series, where x = 5, 10, 15, 20 and 30 mole %.
Boroxol ring \((B_3O_{4.5})\)

Triborate \((B_3O_5^-)\)

Pentaborate \((B_5O_{13}^-)\)

Tetraborate \((B_8O_{13}^{2-})\)

Figure B-6: Superstructural units found in borate glasses.
Diborate ($\text{B}_4\text{O}_{7}^{2-}$)

Di-triborate ($\text{B}_3\text{O}_{5.5}^{2-}$)

Di-pentaborate ($\text{B}_5\text{O}_{8.5}^{2-}$)

Metaborate ring ($\text{B}_3\text{O}_6^{3-}$)

Metaborate chain ($\text{B}_3\text{O}_6^{3-}$)

Pyroborate ($\text{B}_2\text{O}_5^{4-}$)

Figure B-6: Superstructural units found in borate glasses (cont).
Orthoborate ($\text{BO}_3^{3-}$)

Figure B-6: Superstructural units found in borate glasses (cont).
Table B-1: Measured compositions and the dissolution rates in DI water at 37°C for glasses in the Na$_2$O-CaO-B$_2$O$_3$ system. Measured using aliquots from 30mg glass in 50mL of water.

<table>
<thead>
<tr>
<th>Nominal composition</th>
<th>Na$_2$O (mole%)</th>
<th>CaO (mole%)</th>
<th>B$_2$O$_3$ (mole%)</th>
<th>k (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/5/90-EtOH wash</td>
<td>5.4</td>
<td>5.0</td>
<td>89.6</td>
<td>0.320</td>
</tr>
<tr>
<td>5/5/90- no wash</td>
<td>5.3</td>
<td>5.1</td>
<td>89.6</td>
<td>0.382</td>
</tr>
<tr>
<td>10/10/80</td>
<td>10.1</td>
<td>9.1</td>
<td>80.8</td>
<td>0.080</td>
</tr>
<tr>
<td>15/15/70</td>
<td>14.7</td>
<td>14.9</td>
<td>70.4</td>
<td>0.026</td>
</tr>
<tr>
<td>20/20/60</td>
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<td>19.6</td>
<td>61.1</td>
<td>0.041</td>
</tr>
<tr>
<td>0/35/65</td>
<td>0.0</td>
<td>35.4</td>
<td>64.6</td>
<td>0.010</td>
</tr>
<tr>
<td>7.5/27.5/65</td>
<td>7.3</td>
<td>26.9</td>
<td>65.9</td>
<td>0.014</td>
</tr>
<tr>
<td>15/20/65</td>
<td>14.2</td>
<td>20.3</td>
<td>65.5</td>
<td>0.028</td>
</tr>
<tr>
<td>20/15/65</td>
<td>19.5</td>
<td>14.9</td>
<td>65.6</td>
<td>0.029</td>
</tr>
<tr>
<td>27.5/7.5/65</td>
<td>27.2</td>
<td>7.3</td>
<td>65.5</td>
<td>0.140</td>
</tr>
<tr>
<td>35/0/65</td>
<td>34.7</td>
<td>0.0</td>
<td>65.3</td>
<td>very fast</td>
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</tbody>
</table>
APPENDIX C

SUPPLEMENTAL INFORMATION FOR SPECTROSCOPIC STUDY OF THE STRUCTURE OF TERNARY ALKALI-ALKALINE EARTH-BORATE GLASSES
Figure C-1: Raman spectra, measured with a 488nm laser, for the $x\text{Na}_2\text{O}-x\text{MgO}-(100-2x)\text{B}_2\text{O}_3$ series, where $x=10, 15$ and $20$ mole %.
Figure C-2: Raman spectra, measured with a 488nm laser, for the xNa$_2$O-xSrO-(100-2x)B$_2$O$_3$ series, where x = 10, 15 and 20 mole %.
Figure C-3: Raman spectra, measured with a 488nm laser, for the $x\text{Na}_2\text{O} - x\text{BaO} - (100-2x)\text{B}_2\text{O}_3$ series, where $x = 10, 15$ and $20$ mole %. 
Figure C-4: Raman spectra, measured with a 488nm laser, for the 10Li$_2$O-10R'O-80B$_2$O$_3$ series, where R' = Mg, Ca and Sr.
Figure C-5: Raman spectra, measured with a 488nm laser, for the 10R$_2$O-10MgO-80B$_2$O$_3$ series, where R= Li, Na and K.
Figure C-6: Raman spectra, measured with a 488nm laser, for the 10R$_2$O-10SrO-80B$_2$O$_3$ series, where R= Li, Na and K.
Figure C-7: Raman spectra, measured with a 488nm laser, for the 15Na$_2$O-15R’O-70B$_2$O$_3$ series, where R’= Mg, Ca, Sr and Ba.
Figure C-8: Raman spectra, measured with a 488nm laser, for the 20Na$_2$O-20R’O-60B$_2$O$_3$ series, where R’= Mg, Ca, Sr and Ba.
APPENDIX D

SUPPLEMENTAL INFORMATION FOR DISSOLUTION BEHAVIOR OF TERNARY ALKALI-ALKALINE EARTH-BORATE GLASSES
Figure D-1: Dissolution rate data fit for $10\text{Na}_2\text{O}-10\text{MgO}-80\text{B}_2\text{O}_3$ in SBF at 37°C fit using the CVM $[1-(1-\alpha)^{(1/3)}]$ or 3D $[1-(1-\alpha)^{(1/3)}]^2$. 
Figure D-2: Dissolution rate data fit for 10Na$_2$O-10CaO-80B$_2$O$_3$ in SBF at 37°C fit using the CVM \([1-(1-\alpha)^{(1/3)}]\) or 3D \([1-(1-\alpha)^{(1/3)}]^2\).
Figure D-3: Dissolution rate data fit for 10Na$_2$O-10SrO-80B$_2$O$_3$ in SBF at 37°C fit using the CVM [1-(1-$\alpha$)$^{(1/3)}$] or 3D [1-(1-$\alpha$)$^{(1/3)}$]$^2$. 

\[ y = 0.054x \]

\[ R^2 = 0.968 \]

\[ y = 0.018x \]

\[ R^2 = 0.926 \]
Figure D-4: Dissolution rate data fit for $15\text{Na}_2\text{O}\cdot15\text{CaO}\cdot70\text{B}_2\text{O}_3$ in SBF at $37^\circ\text{C}$ fit using the CVM $[1-(1-\alpha)^{(1/3)}]$ or 3D $[1-(1-\alpha)^{(1/3)}]^2$. 

**Graph:**
- **CVM:** $y = 0.072x$, $R^2 = 0.928$
- **3D:** $y = 0.058x$, $R^2 = 0.951$
Figure D-5: Dissolution rate data fit for 20Na₂O-20CaO-60B₂O₃ in SBF at 37°C fit using the CVM \[1-(1-\alpha)^{(1/3)}\] or 3D \[1-(1-\alpha)^{(1/3)}\]^2.
APPENDIX E

SUPPLEMENTAL INFORMATION FOR COMPOSITIONAL DESIGN OF BORATE-BASED BIOACTIVE GLASSES
Table E-I: Glass compositions for the seven component mixture model designed using Design Expert 8. For melt results: c=crystallized on cooling, ps=phase separated, q=melt was quenched with a steel plate to form a glass, and g=glass formed on cooling.

<table>
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<th>glass</th>
<th>B$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>CaO</th>
<th>P$_2$O$_5$</th>
<th>SiO$_2$</th>
<th>melt results</th>
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<td>1</td>
<td>45.00</td>
<td>1.50</td>
<td>12.27</td>
<td>1.91</td>
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<td>5.00</td>
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<tr>
<td>2</td>
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<td>15.04</td>
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Figure E-1: Viscosity curve for 1393-B3 based on a MYEGA fit to the measured data.
Table E-2: Reaction rates of the glasses from “Compositional designing of borate based bioactive glasses.” Model type indicates which kinetic model best fit the data.

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VITA

Kathryn L. Goetschius was born in Wellsville, NY. She graduated from Wellsville High School in 2002. She received a B.S. degree in Glass Engineering and Science from Alfred University in May 2006 with minors in Materials Science, Chemistry and Biology.

After Alfred University, Kathryn worked for two years in the Glass Research Department at Corning Incorporated. From her work there she was granted two patents: Photomachinable glass compositions having tunable photosensitivity (US 7799711) and Low CTE photomachinable glass (US 7829489).

Kathryn left Corning to pursue a Master’s degree in Glass Science. Her research was in the design of a glass composition for neutron detection. These glasses included silicates, borates and germanate based compositions with gadolinium as the neutron capture element. Her work at Alfred University led to three presentations, with one being at an international conference. She was granted her degree in December 2009.

After that, in January 2010, Kathryn joined Dr. Brow’s group at Missouri University of Science and Technology to pursue a Doctorate degree. She received a Fellowship from the Department of Education’s Graduates in Areas of National Need (GAANN) program. Her doctoral work led to four peer-reviewed journal papers, four presentations (two international), and four posters (two international). She was also awarded three travel scholarships to attend international conferences, the SanCAS-MSE, Sao Carlos, Brazil (March 2012), Functional Glasses: Properties and Applications for Energy & Information, Siracusa, Italy (January 2013), and the DGG-GOMD, Aachen, Germany (May 2014). In December 2014, she received her PhD in Materials Science and Engineering from Missouri University of Science and Technology.