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Glass-forming ability of soda lime borate liquids

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1. Introduction

Inorganic glasses are predominantly produced using the melt-quenching technique, where the batch materials are heated to a temperature above the liquidus temperature and then cooled sufficiently fast to avoid crystallization [1–3]. In order to optimize the glass production process, it is important to know the glass-forming ability (GFA) of the melt. The GFA has been systematically investigated for a range of silicate [4], aluminosilicate [5], borosilicate [6], alkali borate [7], and alkaline earth borate [6] liquids. Traditionally borate glasses have found only limited applications due to their poor chemical durability, but recently it has been found that borate glass nanofibers are bioactive and promote the healing of flesh wounds [8]. Hence, it has become increasingly important to understand the GFA of more complex borate liquids. To the best of our knowledge, the GFA of alkali alkaline earth borate liquids has not received much attention. Moreover, the so-called boron anomaly makes the structural foundation of borate glass and liquid properties especially interesting. In borate compositions, the initial addition of alkali or alkaline earth oxides affects properties differently compared to further additions of these same modifiers due to conversion of boron between three-fold (trigonal) coordination and four-fold (tetrahedral) coordination [9]. Hence, the effect could also cause an "anomalous" composition dependence of GFA, and it may thus be particularly interesting to explore this effect [7,9,10]. In this paper, we therefore attempt to quantify and understand the GFA of a series of soda lime borate compositions and connect these results back to general features of glass formation in inorganic liquids.

GFA is a measure of how easily a melt is vitrified and can be quantified by determining the critical cooling rate \( q_c \) [1], which is defined as the minimum cooling rate required to vitrify a melt, i.e., to obtain a glass with a crystal concentration lower than a certain standard value such as 1 ppm. However, it is difficult and time-consuming to determine \( q_c \) precisely, and therefore alternative methods for quantifying GFA have been developed. For example, various glass stability (GS) parameters have been proposed [6,11]. Generally speaking, these parameters all describe the ability of a glass to bypass crystallization upon heating. It has been found that GFA and GS parameters have a direct relationship [4,5], i.e., GS increases with increasing GFA. While there are several proposed metrics for GS, the Hruby parameter \( K_H \) shows a better correlation with GFA compared with other parameters [12]. Therefore, we use \( K_H \) as a measure of GFA in this work. \( K_H \) can be calculated from three characteristic temperatures:

\[
K_H = \frac{T_c - T_m}{T_m - T_g} \tag{1}
\]

where \( T_m \) is the onset transition temperature, and \( T_c \) and \( T_m \) are the onset temperatures of the crystallization peak and the melting peak during heating. A high value of \( K_H \) indicates high glass stability. These characteristic temperatures can be determined experimentally using...
differential scanning calorimetry (DSC). A typical DSC curve for a glass exhibiting high tendency for crystallization has three well-defined characteristic peaks upon heating: an endothermic glass transition peak, an exothermic crystallization peak, and an endothermic melting peak (Fig. 1). $T_g$, $T_c$, and $T_m$ are the onset temperatures of these three peaks, which are determined as the intersection of tangents to the curve, traced on the baseline and on the peak side (Fig. 1). This method is called the "tangent method" [13] and it has its limitations due to the uncertainty in drawing tangents along the sides of the DSC peaks. The inherent drawbacks of using the GS parameters such as $K_t$ are discussed later in this paper.

Shear viscosity of glass-forming liquids is an important temperature-dependent property governing glass formation [14]. It is also related to the GFA, since the flow behavior determines the kinetic activation barriers for both nucleation and crystal growth [6]. Several models have been proposed for describing the temperature dependence of the viscosity ($\eta$) of a melt, e.g., Vogel–Fulcher–Tammann (VFT) [15] and Avramov–Milchev (AM) [16]. However, these models exhibit systematic error when extrapolating to low temperatures as described elsewhere [17]. Recently, based on energy landscape analysis and the temperature-dependent constraint model for configurational entropy [18–20], Mauro et al. have derived a new three-parameter viscosity model [17]:

$$\log \eta = \log \eta_0 + K \exp \left( \frac{C}{T} \right)$$

(2)

where $\eta_0$ is the high-temperature viscosity limit and $K$ and $C$ are constants. This model has been shown to provide improved fitting quality of measured viscosity–temperature curves compared to the existing models. Furthermore, it provides a physically realistic description of liquid dynamics across the full range of temperatures [17,21]. Based on the analysis in [17,21], it has been concluded that $\eta_g$ is a universal composition-independent constant equal to approximately $10^{12}$ Pa s for oxide glasses [22], $\log \eta_g - \log \eta_0 = 12$ (–3) = 15. Eq. (2) can then be expressed in terms of the liquid fragility index $m$ and $T_g$:

$$\log_{10} \eta(T) = -3 + 15 \frac{T_g}{T} \exp \left[ \left( \frac{m}{15} - 1 \right) \left( \frac{T_g}{T} - 1 \right)^{-1} \right].$$

(3)

The definition of the fragility index $m$ is due to Angell [3], who noted that liquids can be classified as either "strong" or "fragile" depending on whether they exhibit an Arrhenius or super-Arrhenius scaling of viscosity with temperature, respectively. The slope of the Angell curve (log $\eta$ as a function of $T_g$ scaled inverse temperature ($T_g/T$)) at $T_g$ defines the fragility index,

$$m = \frac{\partial \log_{10} \eta}{\partial \left( \frac{T_g}{T} \right)} |_{T = T_g}.$$  

(4)

An inverse correlation between fragility index and GFA has been found for various metallic glass-forming liquids in addition to some silicate liquids [23,24]. "Strong" melts have a more consistently rigid structure upon temperature changes compared to "fragile" melts. This rigidity could create steric hindrance towards crystallization during cooling, and therefore strong melts are expected to have better GFA. However, it remains unknown if and how the fragility of borate liquids is correlated with their GFA. Clarifying this relation is one of the objectives of the current study, where we characterize the GFA of these systems by determining their crystallization tendency and viscous flow behavior. We also demonstrate a dramatic enhancement of the glass stability against crystallization for two of the high-Na$_2$O compositions under study after imposing a new thermal history on these glasses. Finally, we discuss the possible structural origin of the enhancement of glass stability.

2. Experiments

2.1. Sample preparation

Eight glass samples were synthesized using analytical reagent-grade H$_2$BO$_3$ (Sigma-Aldrich, ≥99.5%), Na$_2$CO$_3$ (Sigma-Aldrich, ≥99.5%), CaCO$_3$ (Fluka, ≥99%), and Fe$_2$O$_3$ (Aldrich, ≥99.9%) powders. Seven of them have the compositions (mol%) of xNa$_2$O-10CaO-(89-x)B$_2$O$_3$-Fe$_2$O$_3$ with $x$ = 5, 10, 15, 20, 25, 30, and 35. The eighth glass has a composition (mol%) of 25Na$_2$O-10CaO-65B$_2$O$_3$ (denoted B-Na25). The thoroughly mixed batches were melted in a covered Pt$_{90}$Rh$_{10}$ crucible at 1323–1423 K for ~15 min in an inductively heated furnace. Melting by using a covered crucible and the relatively low melting temperatures and short times were chosen to minimize boron evaporation, and homogeneity was ensured by the convection currents created in the melt due to the induction furnace. In order to obtain glasses, the melts were cast onto a brass plate and cooled in air to room temperature. Measurements of the weight loss due to melting indicate that the glasses are within 1–2 wt.% of the desired compositions [25].

Owing to the hygroscopic character of the borate glasses, all samples were kept in glass or plastic containers with desiccant. All of the glasses under study besides B-Na25 contain 1 mol% Fe$_2$O$_3$, since they have also been used in a parallel study that established the influence of boron speciation on ionic transport [26]. The transport properties were studied using an inward cationic diffusion approach, which requires the presence of a polyvalent element in the glass [27]. Moreover, the structure and topology of these glasses have been studied in [25].

2.2. DSC measurements

For the glass stability investigations, the three characteristic temperatures ($T_g$, $T_c$, and $T_m$) were determined using a calorimetric method as shown in Fig. 1. The differential scanning calorimetry (DSC) measurements were performed with a simultaneous thermal analyzer (STA 449 C Jupiter, Netzsch, Selb, Germany) at a rate of 20 K/min for both up- and downscanning in a purged argon atmosphere. The samples were heated to 1273 K to locate the glass transition, crystallization, and melting peaks. As mentioned earlier, the characteristic temperatures were determined using the "tangent method". This method has uncertainties of approximately ±2 to 3 K.

In order to obtain the heat capacity curves of the standard glass (cooling and heating at 10 K/min), the samples were subjected to two runs of DSC upscans and downscans. The rates of the upscans

![Fig. 1. Typical DSC curve of a glass that easily crystallizes during heating. The procedure for determining the three characteristic temperatures $T_g$, $T_c$, and $T_m$ is illustrated.](image-url)
and downscans were always equal to 10 K/min. The recorded heat flow of the first upscan reflects the enthalpy response of a sample with an unknown thermal history (i.e., an unknown cooling rate experienced by the sample during melt-quenching), whereas that of the second upscan reflects the enthalpy response of the sample with a well-defined thermal history (i.e., a known cooling rate). The standard \( T_g \) is determined from the second upscan curve as the onset temperature of the glass transition peak \[28\]. The isobaric heat capacity \( C_p \) curve for each measurement was calculated relative to the \( C_p \) curve of a sapphire reference material of comparable mass.

2.3. Viscosity measurements

In order to determine the liquid fragility index, viscosity measurements were performed. The low viscosities (approximately \( 10^6 \)–\( 10^7 \) Pa s) were measured using a concentric cylinder viscometer. The viscometer consisted of four parts: furnace, viscometer head, spindle, and sample crucible. The viscometer head (Physica Rheolab MC1, Paar Physica) was mounted on top of a high temperature furnace (HT 7, Scandiaovnen A/S). Spindle and crucible were made of \( \text{Pt-PtRh}_{20} \). The viscometer was calibrated using the National Bureau of Standards (NBS) 710A standard glass. In the high viscosity range (approximately \( 10^{10} \)–\( 10^{13} \) Pa s), the viscosity was measured using micro-penetration viscosimetry with a vertical dialimeter (Model VIS 405, Bähr-Termoanalyse, Hüllhorst, Germany). The precision of the equipment was tested using the Deutsche Glastechnische Gesellschaft (DGG) standard glass I and was found to be within \( \pm 1\% \) of the standard linear viscosities stated in \[29\]. The viscosity of the x = 35 composition could not be measured due to its high tendency for crystallization.

2.4. \( ^{11} \text{B} \) MAS NMR spectroscopy

Boron speciation in glasses depends on thermal history \[30\]. In order to investigate the thermal history dependence of boron speciation and how it affects GFA of the soda-lime borate liquids, we carried out \(^{11}\text{B} \) magic angle spinning (MAS) NMR measurements on selected samples. The NMR spectra were collected at 11.7 T (160.34 MHz resonance frequency) using a 2.5 mm MAS NMR probe and sample spinning at 20 kHz. The data were acquired using a short (\( \pi/12 \)) pulse width of 0.6 μs and 1 s recycle delays. 600 scans were collected; data were processed without line broadening and referenced to an external aqueous boric acid sample (19.6 ppm from BF₃-Et₂O). \(^{11}\text{B} \) MAS NMR spectra were fit using DMFit \[31\], with two trigonal and two tetrahedral line shapes for each spectrum. The trigonal sites were reproduced using second-order quadrupolar broadened line shapes, and a mixture of Gaussian and Lorentzian line shapes was sufficient to fit the 4-fold coordinated boron resonances. The experimental data required at least two distinct 3-fold coordinate boron peaks and one 4-fold coordinated boron resonance. A second 4-fold coordinated peak was added to the simulations to account for minor peaks and one 4-fold coordinated boron resonance. Regardless of the exact number of distinct sites in these glasses, all data were fit using identical methods and thus uncertainties in the fraction of tetrahedral to total boron \( (N_t) \) are on the order of \( \pm 0.2\% \).

2.5. XRD measurements

The resulting crystalline phases after the first DSC scan were determined from X-ray diffraction (XRD) measurements. The quantitative XRD analyses were performed using a PANalytical CUBIX PRO instrument. XRD signals were recorded in the range \( 5^\circ \sim \sim 65^\circ \) with a stepsize of 0.02 and a steptime of 120 sec/step. The X-rays were generated by a Cu Kα target operated at 40 kV and 45 mA. XRD signals were recorded in the range 5°–65° with an unknown cooling rate experienced by the sample during melt-quenching), whereas that of the second upscan reflects the enthalpy response of the sample with a well-defined thermal history (i.e., a known cooling rate). The standard \( T_g \) is determined from the second upscan curve as the onset temperature of the glass transition peak \[28\]. The isobaric heat capacity \( C_p \) curve for each measurement was calculated relative to the \( C_p \) curve of a sapphire reference material of comparable mass.

3. Results

DSC upscans are performed on the borate glass series at a heating rate of 20 K/min to determine the glass stability upon heating. Fig. 2 shows the temperature dependence of the DSC output (in arbitrary units) for the seven glasses. The first endothermic peak is attributed to the glass transition. For the four glasses with \( x = 20, 25, 30, \) and 35, there is an exothermic peak well above \( T_g \), which is attributed to crystallization of the glass. An endothermic crystal melting peak occurs following the crystallization peak \[13\]. No crystallization peak is observed for the three glasses with \( x = 5, 10, \) and 15 during dynamic heating at 20 K/min and therefore \( K_g \) cannot be calculated for those glasses. This implies that these compositions have higher glass stability than the other compositions \[24\]. The determined values of \( T_g \), \( T_m \), and \( \text{Hruby parameter} \ k_h \) are stated in Table 1.

It has been found that GFA and kinetic fragility have an inverse correlation for some glass-forming systems \[23,24\]. Here the question is whether this inverse relation exists for the soda lime borate liquid series. Fragility is traditionally determined from viscosity measurements to obtain the kinetic fragility index \( m \). Besides determining \( m \), we also determine the thermodynamic values, which are associated with thermodynamic fragility for many glass systems, such as the jump in isobaric heat capacity \( (C_p) \) in the glass transition region \[32–34\] and glass transition width \( (\Delta T_g) \) \[35\]. Therefore, another question is whether there is a parallel relation between the kinetic and the thermodynamic fragilities.

The temperature dependence of viscosity obtained from both micro-penetration and concentric cylinder viscometry is illustrated by the Angell plot in Fig. 3. The experimental data are fitted to Eq. (3) \[17\], and the kinetic fragility \( (m) \) is derived from the best-fit of Eq. (3) (see Table 1). We find that \( m \) increases with increasing concentration of \( \text{Na}_2\text{O} \), but after reaching its maximum value at \( x = 25 \), it starts to decrease. For the thermodynamic fragility, we determine the \( C_p \) jump as \( C_{p,jump} = C_{p,pp} \), where \( C_{p,pp} \) and \( C_{p,pp} \) are the isobaric heat capacities for the glass at \( T_g \) and the liquid, respectively, as shown in Fig. 4. \( C_{p,pp} \) is determined as the offset value of the \( C_p \) overshoot above the glass transition range. Another characteristic value is the overshoot value of the glass transition peak, \( C_{p,peak} \). It should be noted that this peak value is not the intrinsic heat capacity of the glass at the peak temperature; instead it is a reflection of the kinetic consequence of the glass transition during upscanning. The glass transition width \( (\Delta T_g) \) is determined as \( T_{g,offset} - T_g \), where \( T_{g,offset} \) is the temperature at the offset of the DSC output (arb. units) versus temperature \( (T) \) during heating at 20 K/min for the glasses with compositions of \( x\text{Na}_2\text{O}–10\text{CaO}–(89–x)\text{B}_2\text{O}_3–1\text{Fe}_2\text{O}_3 \).
of the $C_p$ overshoot. The procedures for determining $C_{pl}$, $C_{pg}$, $C_{p,peak}$, and $\Delta T_g$ are illustrated in the inset of Fig. 4.

The composition dependencies of the values of $C_{pl}$, $C_{pg}$, $C_{p,peak}$, and $\Delta T_g$ are shown in Figs. 5–7, respectively. It can be seen that there is no apparent trend in $C_{pl}$ and $C_{pg}$ with composition (Fig. 5), yet there is a trend in $C_{p,peak}$, $C_{pg}$, and $\Delta T_g$ with composition (Fig. 6). The kinetic fragility (quantified by $m$) shows a positive correlation with the values of $C_{p,peak}$ and $C_{pg}$, and the glass transition width, which are in this work regarded as indirect measures of the thermodynamic fragility. This is expected because fragility is fundamentally a kinetic property, and the glass transition width is a reflection of kinetics (i.e., a steeper viscosity curves gives a more sudden breakdown of ergodicity [35,37]), and the glass transition width is a reflection of kinetics (i.e., a steeper viscosity curves gives a more sudden breakdown of ergodicity [35,37]). The kinetic fragility is apparently lost for these borate glasses. In Section 4.2, we will discuss whether there is a correlation between fragility and GFA.

Interestingly, two of the glasses under study (with $x = 20$ and 25) do not exhibit any crystallization exotherms during the second DSC upscan at 20 K/min to 1273 K when they have been subjected to a prior upscan to 1273 K at 20 K/min and a subsequent downscan at the same rate. The DSC curves for the glass with $x = 20$ are shown in Fig. 8(a). The same phenomenon is also observed when the second upscan rate is lowered to 10 K/min (Fig. 8(b)). This means that the stability of these two glasses against crystallization is dramatically enhanced after they undergo a slow cooling process. The enhancement of the glass stability can also be observed in glasses containing higher Na$_2$O content, e.g., glasses with $x = 30$ and 35 as shown in Fig. 9. The glass with $x = 30$ shows a crystallization peak during the first downscan at 20 K/min. This implies that the cooling rate is lower than the critical cooling rate, and hence the melt crystallizes during cooling. After cooling, the sample contains both glass and crystal phases. In the second upscan, there is no crystallization peak, indicating that the remaining glass phase does not crystallize during the second upscan. In other words, the GS of the remaining glass is enhanced after the first downscan. The glass with $x = 35$ shows similar behavior to that with $x = 30$.

We have also determined the crystal phases of the sample with $x = 20$ resulting from the first DSC upscan. This was done by conducting X-ray diffraction (XRD) measurements on samples that were heated in a muffle furnace by using the same conditions as during the DSC scan. As shown in Fig. 10, the sample that has been heat treated contains both crystalline and glassy phases. Using the Rietveld refinement method with an internal standard, the amounts of crystalline and glassy phase are determined to be 56 and 44 wt.%, respectively. The main crystalline phase (97.7 wt.%) is calcium sodium pentaborate, which consists of complex metaborate sheets with a pentaborate, which consists of complex metaborate sheets with a $B_5O_9$ building block. The $B_5O_9$ unit contains BO$_4$ and BO$_3$ groups in a pentaborate, which consists of complex metaborate sheets with a $B_5O_9$ building block. The $B_5O_9$ unit contains BO$_4$ and BO$_3$ groups.

### Table 1
Characteristic temperatures, $K_{HT}$, $N_{4H}$, NBO/B, and $m$ of the seven glasses (xNa$_2$O–10CaO–(89–x)B$_2$O$_3$–1Fe$_2$O$_3$). The errors in the characteristic temperatures are approximately ±2–3 K and uncertainties in $N_{4H}$ are on the order of ±0.2.

<table>
<thead>
<tr>
<th>Sample ($x$)</th>
<th>$T_g$ (K)</th>
<th>$T_m$ (K)</th>
<th>$N_{4H}$ (at%)</th>
<th>NBO/B</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>728</td>
<td>n/a</td>
<td>n/a</td>
<td>16</td>
<td>0.197 ± 49±1</td>
</tr>
<tr>
<td>10</td>
<td>764</td>
<td>n/a</td>
<td>n/a</td>
<td>24</td>
<td>0.266 ± 59±1</td>
</tr>
<tr>
<td>15</td>
<td>774</td>
<td>n/a</td>
<td>n/a</td>
<td>36</td>
<td>0.316 ± 63±1</td>
</tr>
<tr>
<td>20</td>
<td>772</td>
<td>979</td>
<td>1062</td>
<td>40</td>
<td>0.47 ± 67±2</td>
</tr>
<tr>
<td>25</td>
<td>760</td>
<td>954</td>
<td>1055</td>
<td>46</td>
<td>0.63 ± 74±1</td>
</tr>
<tr>
<td>30</td>
<td>742</td>
<td>887</td>
<td>978</td>
<td>43</td>
<td>0.926 ± 65±2</td>
</tr>
<tr>
<td>35</td>
<td>715</td>
<td>824</td>
<td>1118</td>
<td>42</td>
<td>1.247 ± n/a</td>
</tr>
</tbody>
</table>

### Figure 4
Glass transition of the glasses (xNa$_2$O–10CaO–(89–x)B$_2$O$_3$–1Fe$_2$O$_3$) determined by DSC at a heating rate of 10 K/min subsequent to a cooling rate of 10 K/min. The plots are shown as the isobaric heat capacity ($C_p$) divided by $T_g$ at $T_g$ ($C_p/C_p(T_g)$) against $T_g$.

### Figure 5
The step change in the heat capacity ($C_{pl}$–$C_{pg}$) at the glass transition as a function of Na$_2$O content ($x$) for the four glasses with $x = 20$, 25, 30, and 35. In general, the GFA decreases with increasing substitution of Na$_2$O for...
B2O3. To understand this trend, the fractions of tetrahedral boron to total (N4) and NBO/B are determined and listed in Table 1, where NBO/B is the average number of non-bridging oxygens per boron tetrahedron or triangle. With the values of N4, we are able to calculate the number of NBOs per boron. The boron itself can be tetrahedral or trigonal. As shown in Table 1, K4 decreases as the NBO/B increases for \( x = 20, 25, 30, \) and 35. The K4 values of glasses with \( x = 5, 10, \) and 15 are unknown higher values, but we suppose that the GFA increases as the value \( x \) decreases, i.e., NBO/B decreases. An increase of NBO/B lowers the connectivity of the network, which creates escape channels for the moving particles [39]. Consequently it is easy for the particles to rearrange, and hence there may be a greater tendency for crystallization. However, following Phillips–Thorpe constraint theory, we note that a sufficiently low value of NBO/B would also promote crystallization, since rigid structures would then easily percolate throughout the system resulting in crystallization [19,20].

Fig. 11(b) shows N4 and NBO/B as a function of Na2O concentration for all seven glasses. The results indicate that the GFA is closely related to the degree of network connectivity [19]. Boron speciation also has a direct influence on the connectivity. However, N4 does not show a direct relation with K4. There is apparently an influence of both NBO/B and N4 on GFA, since both of these parameters affect the degree of network connectivity. This indicates that when comparing two glasses with different amounts of network former, NBO/B plays a determining role in controlling GFA, while the boron speciation plays a less important role. However, when comparing two glasses with the same amount of network former, the N4 will play an important role, as will be discussed in Section 4.3.

For three of the glasses under study, the Hruby parameter could not be determined, since no crystallization was observed during heating at the applied rates (10 and 20 K/min). It should be noted that the phase transitions observed during a DSC scan are dynamic, i.e., the characteristic temperatures are dependent on the heating rate employed during the measurements. Especially for glasses with high stability (e.g., \( x = 5, 10, 15 \)), the crystallization and melting processes can be bypassed when using a sufficiently high heating rate. For good glass formers, \( K_H \) cannot be determined using the accessible heating rates of a DSC since no crystallization peak is observed. However, theoretically \( K_H \) must have a finite value that could be determined using a sufficiently low heating rate beyond the DSC heating rate window. This highlights the limitation of the Hruby parameter with the current DSC techniques. Actually there are several other GS parameters, e.g., \( K_T, K_W, K_H \) [4,5], which all use the same characteristic...
temperatures, i.e., Tg, Tc, and Tm. Here, we have only shown the results of the representative Hruby parameter, since the other parameters show similar trends. However, the inherent limitations of the Hruby parameter represent a universal drawback for any GS parameter, which includes characteristic temperatures. Therefore, a more universal GFA parameter which can be applied to any glass-forming liquid is needed.

4.2. Relationship between Fragility and GFA

In our attempt to understand the composition dependence of GFA for soda-lime borate liquids, we will investigate the possible correlation between fragility and GFA. However, for this correlation to be insightful, it is important first to understand the composition dependence of fragility. We obtain this understanding from topological constraint theory [19,20], since Gupta and Mauro [9,18] have developed a new topological modeling approach that enables accurate prediction of the scaling of both glass transition temperature and fragility with composition. A key feature of the approach is the incorporation of temperature-dependent constraints that become rigid as a liquid is cooled. Recently, Smedskjaer et al. have extended the topological modeling approach to soda-lime borate systems [25]. The basic three steps to apply the topological modeling approach are: (1) identify and count the number of distinct network forming species (i.e., BO4, B O3, O, and MNB (network modifiers (Na and Ca) that create NBOs); (2) identify and count the number of constraints associated with each species; and (3) calculate fragility in terms of atomic degrees of freedom. Fig. 12(a) shows both the measured and predicted values of m using the topological constraint model (solid line) [25]. The experimental values of m obtained from viscosity measurements are in good agreement with the modeled fragility values.

Four types of bonding constraints are considered in the model: α) B–O and M B–O linear constraints; β) O–B–O angular constraints; γ) B–O–B angular constraints; and μ) additional modifier rigidity due to clustering effects. We note that the borate glasses are intrinsically hygroscopic and thus contain hydroxyl groups that are expected to break linear and angular constraints. This effect is not included in the current model, but the good agreement between data and model predictions of m suggests that neglecting the hydroxyl effect is a good approximation. Fig. 12(b) shows the contribution of each type of constraint to the calculated fragility. m0 is defined as the fragility index of the theoretically strongest liquid, and found to be 15 from Eq. (4).
boron to form a rigid BO₄ tetrahedron and three β constraints per three-fold coordinated boron to keep the BO₃ unit planar [25]. Most importantly, fragility is a first-derivative property and the constraint onset temperature of β constraints is close to Tₚ. Therefore, the derivative of β constraints is large, and these constraints therefore have a large contribution to fragility. Thus, the boron speciation substantially affects fragility.

The indirect measures of the thermodynamic fragility (i.e., Cₚ,peak – Cₚg and glass transition width) both exhibit a positive correlation with kinetic fragility m. The Cₚ,peak – Cₚg measurement is a reflection of both thermodynamics and kinetics, since higher fragility leads to a sharper and more well-defined glass transition [37] and the value of Cₚ,peak is influenced by the kinetic glass transition process. Therefore, m has a positive relation with both Cₚ,peak – Cₚg and the glass transition width.

An inverse correlation between fragility and GFA has been found for various metallic glasses [24,40], and hence fragility can be used as a quantitative measure of GFA for those systems. However, we find that this is not the case for these soda lime borate compositions. Comparing Fig. 12(a) with Fig. 11(a), we can see that fragility and GFA do not exhibit a linearly inverse relation. In addition, the thermodynamic fragility (shown in Figs. 6 and 7) and GFA also do not exhibit this relation. As mentioned above, both NBO/B and boron speciation affects the degree of network connectivity. Within different amounts of network former, NBO/B plays a determining role in controlling GFA, while the boron speciation plays a less important role for GFA. However, when we calculate the fragility with topological constraint theory, the boron speciation is counted, which plays a less important role for GFA in different compositions. In addition, GFA is related to many other properties, e.g., the degree of network connectivity [24], liquidus temperature [14,41], but it is not necessarily related to only fragility [40]. Therefore, GFA and m might not have a linear inverse correlation.

4.3. Enhancement of glass stability

Interestingly, the glass stability becomes enhanced for some of the glasses after the first DSC up- and downscans, as shown in Figs. 8 and 9. Now the question arises: what is the origin of the enhancement of the GS after slow cooling? To answer this question, we discuss several factors which could affect the crystallization behavior of these glasses.

For borate systems, liquid-liquid phase separation is often an issue to consider [42]. Phase separation could occur during the first DSC upscan, since phase separation is more favorable at higher temperatures due to the supplementation of thermal energy. Hence, the atoms more easily overcome the energy barriers to rearrange and favor phase separation [1]. If phase separation has occurred, there will be two glassy phases and during the second DSC upscan, the Tₕ and the Cₚ jump should have changed and a second glass transition peak should have been observed. However, we did not observe these changes and we therefore exclude this factor. Moreover, the enhancement of GS is likely not attributed to the evaporation of boron during the DSC scans. Boron vaporizes rapidly when the temperature is above 1473 K [43], but the sample was only scanned to 1273 K. and therefore the temperature was low enough to exclude significant boron evaporation. Another possible explanation could be that during the first upscan, the glass disk was inserted in the Pt crucible with relatively poor contact between glass and Pt crucible. However, during the second upscan, the sample stuck to the Pt-crucible due to the melting during the first upscan. The heat transfer was then more efficient during the second upscan, since there is minimal air gap between the sample and the bottom of the Pt crucible. In order to explore this possible explanation for a change in GS, we melted the glass inside the Pt-crucible in the induction furnace and then performed the DSC scan. We observed the same phenomenon, i.e., the enhancement of GS first occurs during the second upscan. Thus, we can also exclude any effects related to the surface contact between glass and crucible.

Instead, the enhancement of GS might be related to the temperature dependence of the boron speciation. Temperature-induced changes in boron speciation have been reported in alkali borate glasses and melts [44,45]. According to these previous studies, the fraction of BO₄ tetrahedra decreases with increasing temperature above Tₛ, indicating that the BO₄ tetrahedra in the glass are converted to BO₃ triangles in the melt [44]. The BO₃ to BO₄ conversion can lower the rigidity of the glasses, since the degree of cross-linking of the borate framework with covalent B-O bonds is lowered [44]. According to [25], there are five β constraints (O-B-O angular constraints) per B³ to form a rigid BO₄ tetrahedron and three β constraints per B³ to keep the BO3 unit planar. Thus, the glass containing more BO3 has a less rigid network structure. In other words, the degrees of freedom of the liquid at the crystallization temperature increase with increasing BO3 concentration. This facilitates rearrangement of the structural units, and hence crystallization. Consequently, the glass stability is lowered. In Section 4.1 we mentioned that in glasses with different amount of network former, NBO/B plays a determining role in controlling GFA, while the boron speciation plays a less significant role. However, considering a constant concentration of network former, the boron speciation conversion will have a significant effect. An increase of N₄ after the first upscan will result in a decrease of NBO, which is expected to cause an increase of GS. Therefore, this combination of two effects should lead to a substantially enhanced GS.

The concentrations of BO₃ and BO₄ in a borate glass depend on the cooling rate that the borate melt experienced during production, i.e., its thermal history [46–49]. The GFA is ultimately determined during this cooling process. The as-produced glasses studied here have been subjected to a relatively fast cooling (approximately 1000 K/s [50]). After the first DSC upscan, the melt was cooled at a slower rate, i.e., 0.17 K/s. The higher the cooling rate, the higher fraction of BO3 is frozen-in. Upon re-heating, the rapidly cooled glass should crystallize more easily than the slowly cooled glass due to the factors mentioned above. In order to test whether these inferences are reasonable, ¹¹B MAS NMR measurements have been conducted on the Fe-free glass (B-Na25) before and after the first upscan. We choose an iron-free analogous glass in order to avoid the effect of dipolar coupling between ¹¹B nuclear spin and unpaired spin of d-electrons in Fe during the NMR measurement. As shown in Fig. 13, the N₄ values for the glass before and after the first upscan are 46.3 and 47.8 at%, respectively. For relatively fast cooling (before first upscan), more BO3 species are frozen-in and the N₄ value is low. For a slower cooling (after first upscan), less BO3 species are frozen-in and N₄ attains a higher value. N₄ increases by 1.5 at% after the first up- and downscans. This provides evidence for the possible link between the boron speciation and the enhanced GS.
5. Conclusions

The glass forming ability (GFA) of a series of soda lime borate liquids has been determined using a calorimetric method. Specifically, we express GFA in terms of the Hruby parameter. It is found that GFA decreases when Na2O is substituted for B2O3, implying that the network connectivity greatly controls GFA of the studied systems. We note that the applicability of the Hruby parameter is limited only to the poor glass formers. The inverse correlation between liquid fragility and GFA, which has been found for some glass-forming liquid series, is not observed for these systems. We also report a remarkable enhancement of GFA can be attributed to the structural conversion of BO3 units into BO4 units during this slow cooling process. This conversion increases the network connectivity of the glass, and hence the GFA.

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References