Glass Formation by Rapid Quenching in Lithium Silicates
Containing Large Amounts of Li$_2$O

Masahiro TATSUMISAGO, Tsutomu MINAMI and Masami TANAKA*

Department of Applied Chemistry, University of Osaka Prefecture
Department of Applied Chemistry, Kinki University

The rapid-quenching technique extended the glass-forming region in the system Li$_2$O-SiO$_2$ toward the composition with high Li$_2$O content. The ratio of the glass transition temperature $T_g$ to the liquidus one $T_l$ deviates largely from the so-called “two thirds rule” ($T_g/T_l=2/3$) in the glasses containing large amounts of Li$_2$O. The deviation was observed only in the glasses prepared by rapid quenching and it can be attributed to their high liquidus viscosity or small temperature variation of viscosity. The relation between the deviation from the “two thirds rule” and the glass-forming ability was discussed on the basis of the temperature and time variation curves of viscosity.

[Received March 25, 1985]

Key-words: Glass formation, Rapid quenching, Two thirds rule, Critical cooling rate, Lithium silicate, Li$_2$O-SiO$_2$ system

The rapid quenching technique is proved useful to extend glass-forming regions and to develop new glass-forming systems. This technique made it apparent that the glass-forming ability of materials could not be determined by only their components and compositions, which were the most important factors in the classical glass formation theories. Kinetic approach in which both the cooling rate and the crystallization rate are considered, is shown to be essential to estimate the glass-forming ability of materials. In addition some favorable conditions such as high liquidus viscosity and large units of viscous flow were presented for glass formation. In those papers, the glass-forming ability is closely related to the viscosity of materials.

We have previously presented a new rapid-quenching apparatus combining a thermal-image furnace and a twin roller. Glass formation was tested for the Li$_2$O-SiO$_2$ system by using this apparatus. In this system, the limit of glass formation was extended up to 66.7 mol% Li$_2$O, corresponding to the composition of lithium orthosilicate Li$_4$SiO$_4$, from 40 mol% Li$_2$O in the usual procedure.

One of the remarkable features of such glasses containing extremely large amounts of Li$_2$O is their glass structure constructed not by a “network” but by discrete silicate anions only, such as SiO$_4^{4-}$ and Si$_2$O$_7^{6-}$. Such a glass structure without “network” shows a striking contrast to classical glass formation theories. In addition some of these glasses do not follow the empirical rule, $T_g/T_l=2/3$ referred to as the “two thirds rule”, which holds well for a wide variety of oxide glasses.

In this note, the results of thermal analysis are reported in more detail for the rapidly quenched
Li$_2$O-SiO$_2$ glasses containing large amounts of Li$_2$O. The deviation from the "two thirds rule" and the glass-forming ability of this system are discussed on the basis of the temperature and time variation curves of viscosity in the undercooled state.

The glass preparation technique is similar to that published elsewhere. The glass transition temperature ($T_g$) and the crystallization temperature ($T_c$) were determined by the differential scanning calorimetry (DSC) using a Rigaku Denki thermal analyzer. The lithium content of glasses obtained was determined by atomic absorption analysis using a Hitachi 170-10 atomic absorption spectrophotometer.

Table 1 lists the nominal and analytical compositions, $T_g$, $T_c$, and $T_g/T_1$ for rapidly quenched glasses in the system Li$_2$O-SiO$_2$, where the

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Nominal</th>
<th>Analytical</th>
<th>$T_g/K$</th>
<th>$T_c/K$</th>
<th>$T_g/T_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O/SiO$_2$</td>
<td>40.0</td>
<td>41.3</td>
<td>775</td>
<td>856</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>50.4</td>
<td>687</td>
<td>735,835</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>59.6</td>
<td>543</td>
<td>686</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>66.7</td>
<td>63.0</td>
<td>463</td>
<td>648,749,666</td>
<td>0.33</td>
</tr>
</tbody>
</table>

The values of $T_g$ plotted in Fig. 1 range from 0.33 to 0.51. They decrease with an increase in the Li$_2$O content and deviate more and more from the broken line indicating the ratio $T_g/T_1=2/3$. The largest deviation was observed in the glass 63 Li$_2$O · 37 SiO$_2$. Such a deviation has never been observed in the oxide glasses prepared by the usual quenching. Therefore, the deviation seems to be attributed to the fact that the Li$_2$O-SiO$_2$ glasses in the present study could not be prepared by the usual quenching technique and were prepared only by the rapid quenching. In fact, the rapidly quenched Li$_5$SiO$_4$-Li$_3$BO$_3$ glasses also exhibited the value of $T_g/T_1$ ranging from 0.29 to 0.50, which were too low to be fitted to the "two thirds rule". The large deviation was, however, not always observed in the glasses prepared by the rapid quenching. The values of $T_g/T_1$ of the rapidly quenched R$_2$O-WO$_3$ glasses (R=Li, Na, K) were almost constant and followed
the "two thirds rule"\(^{(3)}\).

The deviation of rapidly quenched glasses is schematically discussed in Fig. 2, where the relation between viscosity \( \eta \) and temperature \( T \) is shown for three hypothetical materials, A, B and C, in the undercooled state. Here, \( T_g \) is assumed to be the temperature corresponding to the viscosity of \( 10^3 \) poise. The material A shows the large temperature variation of viscosity and the material C has the high liquidus viscosity. Both materials exhibit the \( T_g \) value comparable to \( 2T_1/3 \). Most materials for which glass can be prepared by the usual quenching would show the temperature variation of viscosity like the curve A or C because they follow the "two thirds rule". On the other hand, the \( T_g \) value is smaller than \( 2T_1/3 \) in the material B, showing the low liquidus viscosity and the small temperature variation of viscosity. The materials containing large amounts of Li\(_2\)O in the system Li\(_2\)O-SiO\(_2\) must show the temperature variation of viscosity like the curve B because of their small values of \( T_\theta/T_1 \). The difficulty is caused by the fact that the material B takes longer time in order to attain the glassy state than the material A or C. This indicates that the material B tends to bring about its crystallized state during quenching in the undercooled state before it attains the glassy state.

The time \( t \) required for cooling the materials from \( T_1 \) to \( T \) can be calculated by dividing the degree of undercooling \( (T_1-T) \) by the cooling rate \( (Q) \), i.e.

\[
t = \frac{T_1-T}{Q}
\]

Using the Eq. (1), the axis of the temperature \( T \) in Fig. 2 can be converted into that of the time \( t \) for a given value of \( Q \). Figure 3 shows the hypothetical viscosity-time curves with the axis of cooling rate \( Q \) as a third one. In the figure, the viscosity-time curves obtained from the viscosity-temperature curves (Fig. 2) by using Eq. (1) are illustrated for three given cooling rates, \( Q_1 \), \( Q_2 \) and \( Q_3 \). It is assumed that \( Q_1 < Q_2 < Q_3 \). The curves \( A_n \) and \( B_n \) given for the materials A and B, respectively, are the viscosity-time curves under the cooling rate \( Q_n \). The curves for the material C were omitted in this figure for simplicity of discussion. If the cooling rate \( Q \) is determined, it is apparent that the material A attains the glassy state \( (10^3 \) poise) earlier than the material B because \( t_{1A} < t_{1B} \) (\( n = 1, 2, 3 \)). As \( Q \) is increased, it takes shorter time needed to reach the glassy state, i.e. \( t_{2A} > t_{2B} > t_{3A} \) and \( t_{2B} > t_{2B} > t_{3B} \). If detectable amounts of crystals form before the glassy state is attained, the material is judged to be crystals. In order to simplify the discussion, it is useful to introduce the crystallization time \( t_c \) which is required to form detectable amounts of crystals in the undercooled melt. Here, \( t_c \) is assumed to be constant; the reasonable value of \( t_c \) is tentatively shown in Fig. 3. The value of \( t_c \) must be at least larger than \( t_{1A} \). The material A showing curve \( A_n \) will attain the glassy state \( (\eta>10^3 \) poise) before the crystallization takes place. In the material B showing curve \( B_n \), however, whether or not the crystallization takes place depends on the cooling rate. The figure shows a case that the moderate cooling rate \( (Q_2) \) happens to be comparable with the critical cooling rate of the material B; under such a rate \( t_{2B} \) becomes nearly equal to \( t_c \). Under the usual cooling rate \( (Q_1) \) crystallization will take place at \( P \) before the undercooled melt attains the glassy state because \( t_{1B} \) is larger than \( t_c \). On the other hand, using the rapid quenching \( (Q_3) \) the undercooled melt attains the glassy state before crystallization takes place because \( t_{3B} \leq t_c \).

Figure 3 tells that the material B, in which \( T_\theta/T_1 \) values deviate largely from the "two thirds
rule" as shown in Fig. 2, could not form glass by the usual quenching procedure. The material B can form glass under the cooling rate like $Q_3$, higher enough than $Q_1$. Therefore, the formation of glasses, for which the deviation from the "two thirds rule" was observed, is responsible for the achievement of large cooling rates by rapid quenching. In other words, the ratio $T_g/T_1$ can be a measure of the glass-forming difficulty. In fact, Davies showed that the critical cooling rate of glassy metals strongly depends on the ratio $T_g/T_1$ dangers to the "two thirds rule" were observed in many glassy metals prepared by rapid quenching.

The small temperature variation of viscosity must be obtained in the rapidly quenched Li$_2$O-SiO$_2$ glasses which deviate from the rule. This feature of the glasses may be related to their unusual glass structure constructed by isolated ions. The "isolated ion" glass structure probably corresponds to the fact that the units of viscous flow are small. The small flow units must lead to the small temperature variation of viscosity and thus to the difficulty of glass formation.

Acknowledgment The authors acknowledge support for this research by a Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, Culture and Science of Japan, and by the Asahi Glass Foundation for Contribution to Industrial Technology.

References