Thermal Expansion of Binary Alkali Silicate Glasses

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The thermal expansions of a number of binary lithium, sodium, and potassium silicate glasses are reported over the temperature range from room temperature to their deformation points. The expansivities of the glasses increased with increasing alkali oxide concentration. These expansivities were used to calculate density values, which were correlated with density measurements in the liquid range. At room temperature the density of each series increased with increasing alkali oxide concentration. With increasing temperature, the density-temperature curves for each binary series crossed each other and the density-concentration order was reversed. This reversal occurred in the lowest temperature range for the lithium silicates, in an intermediate temperature range for the potassium silicates, and in the highest temperature range for the sodium silicates.

1. Introduction

The thermal expansivity of fused silica and of many binary alkali silicate glasses has been studied previously by various investigators using a variety of methods. Karkhanavala [1] has compiled the results of many of these investigations. Most of these studies were concerned with a single binary system of glasses, mainly Na₂O-SiO₂. The present investigation was conducted to show the effect of concentration of alkali oxide on the thermal expansivity of binary silicate glasses. The alkali oxides studied were lithium, sodium, and potassium. The present results are part of a continuing study of various properties of binary alkali silicates. The properties measured previously include surface tension [2], density, expansivity, viscosity [3], and compressibility [4]. This is the second paper on the thermal expansivity of some selected binary glasses, and follows one concerned with the binary alkaline-earth borate glasses [5].

2. Preparation of Glasses and Method of Test

The glasses used in the present investigation were made for the investigations of surface tension [2] and viscosity [3]. They were later remelted for the compressibility study [4]. Following the compressibility study a portion of each glass was removed for analysis. The silica was determined gravimetrically in each case by fusing a sample with sodium carbonate, treating with hydrochloric acid, and removing the silica by the usual double-dehydration procedure. The amount of silica thus obtained was corrected for possible impurities by volatilization with hydrofluoric acid. The alkali content of each sample was calculated by difference. After the sample was cut for analysis, an adjacent portion of each compressibility sample was cut off and shaped into a thermal expansion specimen [5]. Refractive index measurements made on the compressibility specimens before and two days following compressibility measurements indicated that no permanent deformation occurred.

3. Results and Discussion

3.1. Fused Silica

A very thorough discussion of the thermal expansion of fused silica is found in the book by Sosman [7]. A more recent compilation of the data concerning the thermal expansion of fused silica was made by Karkhanavala [1]. Because fused silica is an end member of the systems studied, its expansion was measured from room temperature to 825°C. The results of this work are given in table 1. The density points in figures 2, 4, and 6, at 25°C, 900°C, 1,000°C, and 1,100°C on the fused-silica curve, are those of Sosman [7].

3.2. Lithium Silicates

The results of the measurements of the thermal expansion of the lithium silicate glasses and the end-member fused silica are given in figure 1 and table 1. There is an increase in expansivity with increasing concentration of lithium oxide and with increasing temperature from room temperature to the deformation points [8]. Table 1 shows that the deformation-point temperatures decrease slightly with increasing lithium oxide content.

Figure 2 shows the density-temperature curves for fused silica and the binary lithium silicates. The lower temperature portions of these density-temperature curves were calculated from density measurements at room temperature [4] and the thermal expansion data. This figure also includes density data that were obtained previously in the liquid range [3]. Although it was not possible to obtain density values between the deformation points and 1,100°C, dashed lines are shown that connect data obtained on the same composition. X-ray data on other glasses in this range do not indicate any maxi-

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†Figures in brackets indicate the literature references at the end of this paper.
### Table 1. Linear thermal expansivity of binary alkali silicate glasses

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Density (room temperature)</th>
<th>Deformation point temperature</th>
<th>Average coefficients of expansion per degree C at—°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>room to 100° C</td>
</tr>
<tr>
<td>R₂O</td>
<td>R₂O</td>
<td>(g/cm³)</td>
<td>°C</td>
</tr>
<tr>
<td>Fused SiO₂</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mole %</td>
<td>wt %</td>
<td>2.385 [7]</td>
<td>2.357</td>
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<tr>
<td>32.0</td>
<td>19.0</td>
<td>2.355</td>
<td>483</td>
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<tr>
<td>34.6</td>
<td>20.8</td>
<td>2.348</td>
<td>481</td>
</tr>
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<td>37.8</td>
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<td>2.354</td>
<td>478</td>
</tr>
<tr>
<td>39.6</td>
<td>24.6</td>
<td>2.353</td>
<td>477</td>
</tr>
<tr>
<td>Li₂O—SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.3</td>
<td>21.8</td>
<td>2.384</td>
<td>507</td>
</tr>
<tr>
<td>24.0</td>
<td>24.6</td>
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<td>31.1</td>
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</tr>
<tr>
<td>35.8</td>
<td>35.5</td>
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<tr>
<td>37.2</td>
<td>38.0</td>
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<td>467</td>
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<td>Na₂O—SiO₂</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>17.3</td>
<td>24.7</td>
<td>2.364</td>
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<tr>
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<tr>
<td>31.8</td>
<td>42.2</td>
<td>2.456</td>
<td>454</td>
</tr>
</tbody>
</table>

*The estimated accuracy of measurement is ±0.1X10⁻⁴.

#### Figure 1. Linear thermal expansion of binary lithium silicate glasses and fused silica.

#### Figure 2. Densities of binary lithium silicate glasses and liquids and fused silica as a function of temperature.

Density values in the liquid range were derived from data from Shartsis, Spinner, and Cappe [3] and density values for fused silica are from Sosman [7]. Solid lines are drawn from experimental data, and dashed lines are included to connect experimental data obtained from the same composition.
ma, minima, or discontinuities, and therefore the general form of the curves is believed to be reasonable. The density values at room temperature generally increase with increasing concentration of lithium oxide (except perhaps between 37.9 and 39.6 mole percent of Li$_2$O), whereas at 1,100°C, and above, the reverse is true. As these reversals occur in the unmeasured region their temperatures are uncertain.

3.3. Sodium Silicates

The thermal expansivity data for the binary sodium silicate glasses are given in figure 3 and table 1. Although the thermal expansion of this series of glasses has been measured several times by a variety of methods and with slightly varying results [1], including one time by Schmid, Finn, and Young [9], it was thought advisable to repeat this work so the conditions of measurement would be comparable with the other series of glasses studied in the present investigation. The present determination also permitted direct comparisons on the same compositions with data previously obtained in the liquid range [3].

The expansivity of the binary sodium silicate glasses increased with increasing sodium oxide content. The deformation point temperatures decreased with increasing sodium oxide content.

Figure 4 is similar to figure 2 and shows the density-temperature curves for the binary sodium silicate glasses and liquids. The density values at room temperature increased with increasing concentration of sodium oxide. The order of these curves remains unchanged up to about 1,250°C. In the region from 1,250°C to 1,400°C the curves cross one another. Although one might expect, on the basis of additive property factors [10], that the curves would cross at a point, this does not seem to be the case. The density-temperature curves for the sodium silicates crossed in a higher temperature range (1,250°C to 1,400°C) than did the curves for the lithium silicates (500°C to 1,100°C).

3.4. Potassium Silicates

The thermal expansivity data for the potassium silicate glasses are given in figure 5 and table 1. Figure 5 shows the thermal-expansion curves, and a comparison of these curves shows an increase in expansivity with increased concentration of potassium oxide. Figure 5 also shows three curves for the glass containing 17.3 mole percent of K$_2$O. The additional data were obtained because the first determination (curve A) disclosed a decrease in the slope of the expansion curve just prior to the rapid-expansion region. This decrease was probably indicative of strain [11] and was removed by re-annealing. This strain was not readily detected in the polariscope. Curves A and B were obtained from separate specimens of glass cut from the compressibility sample. Curve C shows the results

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**Figure 3.** Linear thermal expansion of binary sodium silicate glasses.

**Figure 4.** Densities of binary sodium silicate glasses and liquids and fused silica as a function of temperature.

Density values in the liquid range were derived from data from Shartsis, Spinner, and Capps [3] and density values for fused silica are from Sosman [7]. Solid lines are drawn from experimental data, and dashed lines are included to connect experimental data obtained from the same composition.
after the second specimen, B, was reannealed by allowing it to cool in the expansion furnace overnight. This heat treatment of the glass was sufficient to remove the decrease in slope in the expansion curve. The curves for the other glasses shown in this figure are those of similarly reannealed samples. The results of all determinations are included in table 1 and a comparison of the data shows the reproducibility of the coefficient of expansion of two specimens of each of two glasses (17.3 and 27.8 mole percent of K$_2$O) and the change in coefficient of expansion caused by the reannealing.

Figure 6 shows the density-temperature curves for the binary potassium silicates. Values previously determined in the liquid range are included. These curves are similar in arrangement to those for the lithium and sodium silicate series. Although the exact crossing points of the curves were not determined, they seem to be higher than those of the lithium silicates and lower than those of the sodium silicates. The curve for the 17.3 mole percent of K$_2$O composition crosses the others between 1,050° and 1,150° C, and the other curves seem to cross each other about 150 deg C lower.

3.5. Comparison of the Thermal Expansivity of Binary Alkali Silicate Glasses

The average coefficients of expansion of the binary alkali silicate glasses from 50° to 400° C as a function of composition are shown in figure 7. The results of
4. Summary and Conclusions

The thermal expansivity of glasses in three binary alkali silicate series was measured. The expansivity of the binary glasses increased with increasing concentration of lithium, sodium, or potassium oxide. The densities determined from these results were correlated with density values obtained previously in the liquid range in order to study the expansion over a greater temperature range. The change in density per degree Celsius for any given composition was greater in the liquid range than in the solid range. At room temperature the density of each series of glasses increased with increasing alkali oxide concentration. The density-temperature curves for each series crossed each other and the density-concentration order was reversed. This crossing occurred in the lowest temperature range for the lithium silicates, in an intermediate temperature range for the potassium silicates, and in the highest temperature range for the sodium silicates.

5. References


Washington, April 13, 1956.