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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] [1] has compiled the results of many of these investigations. Most of these studies were concerned with a single binary system of glasses, mainly Na_2O-SiO_2. 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.

The measurements of thermal expansion were made by the interferometer method [6]. The furnace was heated at a rate of about 2 deg C per minute from room temperature through the deformation point of the sample under test. The interference fringes were recorded on photographic film and the results were read from this film.

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°, 900°, 1,000°, 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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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Linear thermal expansivity of binary alkali silicate glasses*

Chemical Composition		Density (room temperature)	Deformation point temperature	Average coefficients of expansion per degree C at—*			
R_2O	R_2O			room to 100° C	100° to 200° C	200° to 300° C	300° to 400° C
			Fused SiO_2				
Mole % 0.0	*wt %* 0.0	*g/cm³* 2.203 [7]	*° C* --------	0.54×10^{-6}	0.67×10^{-6}	0.62×10^{-6}	0.62×10^{-6}
			Li_2O–SiO_2				
32.0	19.0	2.337	469	9.52×10^{-6}	10.21×10^{-6}	10.59×10^{-6}	12.06×10^{-6}
34.6	20.8	2.348	483	9.90	11.12	12.00	12.71
37.9	23.3	2.354	491	10.02	11.70	12.68	14.14
39.6	24.6	2.353	477	10.96	12.16	13.14	14.77
			Na_2O–SiO_2				
20.3	20.8	2.384	507	9.75×10^{-6}	9.93×10^{-6}	10.06×10^{-6}	10.69×10^{-6}
24.0	24.6	2.420	499	10.07	11.43	11.66	12.17
31.1	31.8	2.472	490	13.60	14.25	14.89	16.00
33.8	34.5	2.491	479	14.39	16.38	16.91	17.35
37.2	38.0	2.507	467	15.21	16.09	17.16	18.77
			K_2O–SiO_2				
17.3	24.7	2.364 Second specimen Reannealed	525 523 525	10.12×10^{-6} 10.54 10.19	10.23×10^{-6} 10.09 10.05	9.92×10^{-6} 10.09 9.97	9.51×10^{-6} 10.01 10.20
23.2	32.2	2.399 Reannealed	511 510	12.98 12.92	13.04 13.32	13.40 13.14	13.39 13.47
27.8	37.6	2.423 Second specimen Reannealed	453 470 470	15.00 15.09 15.03	15.27 15.23 15.32	14.93 14.33 15.10	14.00 14.17 15.43
31.8	42.2	2.456 Reannealed	-------- 454	15.82 16.35	16.55 16.51	16.43 16.02	----------- 16.54

* The estimated accuracy of measurement is $\pm0.1\times10^{-6}$.

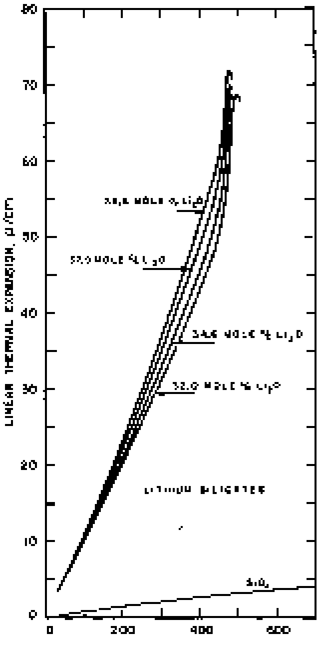

FIGURE 1. *Linear thermal expansion of binary lithium silicate glasses and fused silica.*

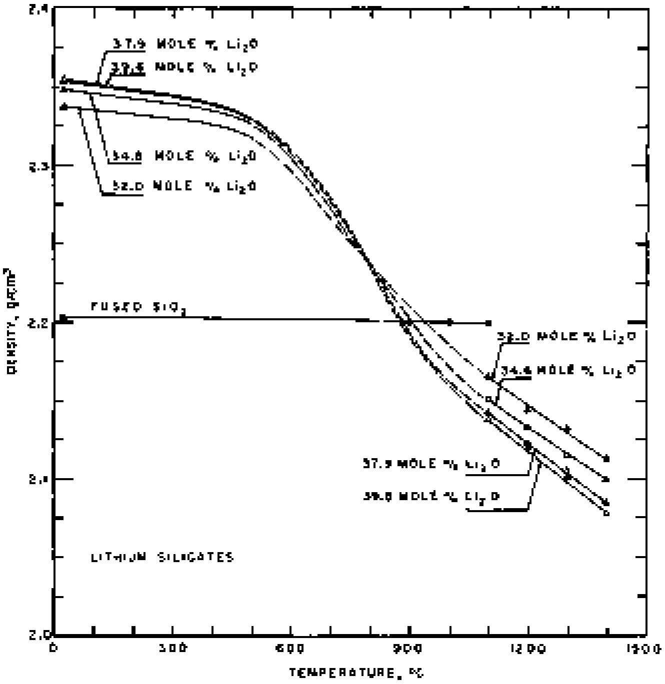

FIGURE 2. *Densities of binary lithium silicate glasses and liquids and fused silica as a function of temperature.*

Density values in the liquid range were derived from data from Shartsis, Spinner, and Capps [8] 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_2O), 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° 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° to 1,400° C) than did the curves for the lithium silicates (500° 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_2O. 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 reannealing. 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

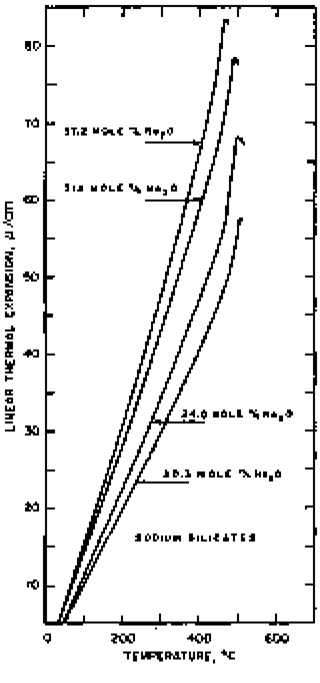

FIGURE 3. *Linear thermal expansion of binary sodium silicate glasses.*

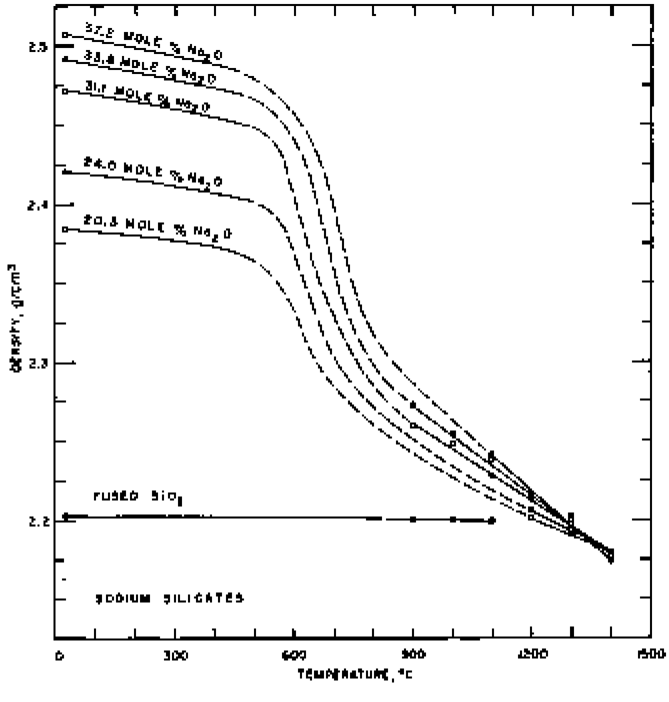

FIGURE 4. *Densities of binary sodium silicate glasses and liquids and fused silica as a function of temperature.*

Density values in the liquid range were derived from data from Shartsis, Spinner, and Capps [3] and density values for fused silica are from Bosman [7]. Solid lines are drawn from experimental data, and dashed lines are included to connect experimental data obtained from the same composition.

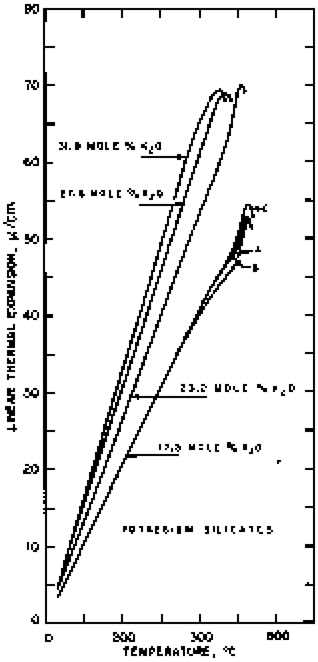

Figure 5. *Linear thermal expansion of binary potassium silicate glasses.*

The three curves for the glass containing 17.3 mole percent of K_2O are: A, sample 1; B, sample 2; and C, sample 2 reannealed.

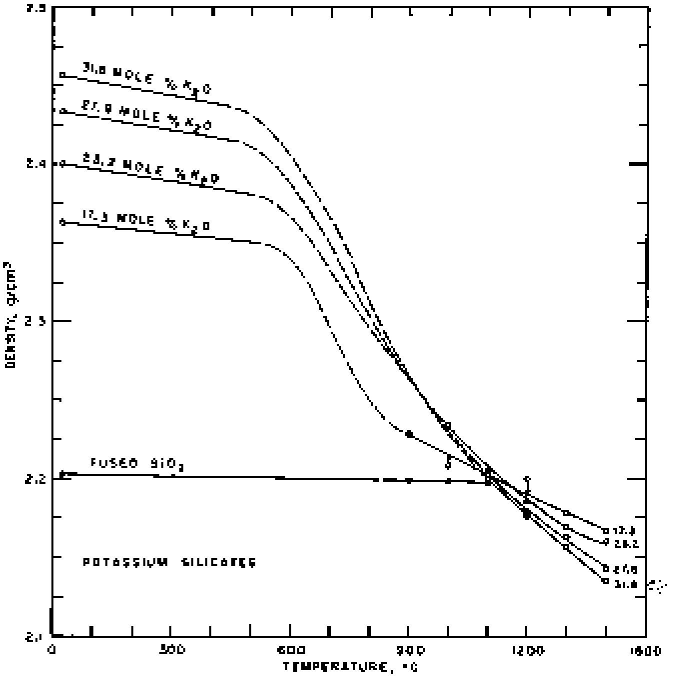

Figure 6. *Densities of binary potassium silicate glasses and liquids and fused silica as a function of temperature.*

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_2O) 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_2O 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

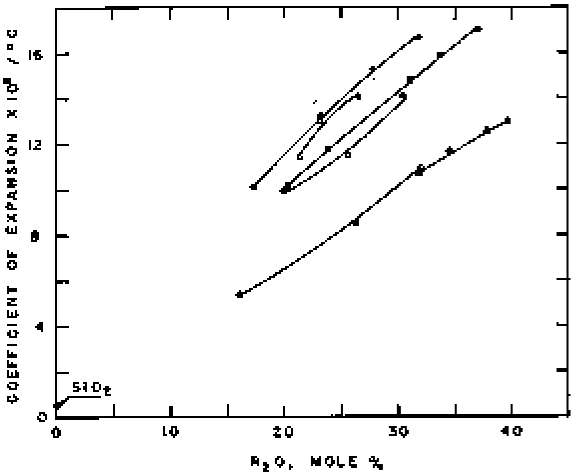

Figure 7. *Average coefficient of expansion of binary alkali silicate glasses and fused silica for the temperature interval 50° to 400° C.*

The triangles indicate lithium glasses; squares indicate sodium glasses; and circles indicate potassium glasses. Closed figures indicate results of the present investigation. These points represent data for a heating rate of 2 deg C/min. Open figures indicate results of Dietzel and Sheybany [11]. Their data were for the temperature interval from room temperature to the transformation point, with a heating rate of 2 to 3 deg C/min.

the present investigation are indicated by the closed figures. The results of a similar investigation by Dietzel and Sheybany [12] are included for comparison. Their results are not truly comparable, as their temperature range was from room temperature to the "transformation point," which varied with composition and had values from 430° to 489° C.

The results in figure 7 indicate an approximately linear relationship between coefficients of expansion and composition. It would be possible therefore to obtain additive expansivity factors such as those compiled by Sun and Silverman [10]. It is doubtful, however, if these factors would apply to other types of glasses. A comparison of the curves for the three binary alkali silicate series indicates that at comparable concentrations the potassium silicate glass has the highest expansivity followed in decreasing order by the sodium and then the lithium glasses.

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

[1] M. D. Karkhanavala, Bibliography of thermal expansion of glasses, Glass Industry **33**, 403–07 (1952).

[2] Leo Shartsis and Sam Spinner, Surface tension of molten alkali silicates, J. Research NBS **46**, 385–90 (1951) RP2209.

[3] L. Shartsis, S. Spinner, and W. Capps, Density, expansivity, and viscosity of molten alkali silicates, J. Am. Ceram. Soc. **35**, 155–60 (1952).

[4] C. E. Weir and L. Shartsis, Compressibility of binary alkali borate and silicate glasses at high pressures, J. Am. Ceram. Soc. **38**, 299–306 (1955).

[5] Herman F. Shermer, Thermal expansion of binary alkaline-earth borate glasses, J. Research NBS **56**, 73–80 (1956) RP2650.

[6] Glassware, laboratory; methods of sampling and testing, Federal Specification DD–G–626a, Coefficient of expansion (interferometer procedure), method No. 241 (23 April 1953).

[7] Robert B. Sosman, The properties of silica, 398–413 (Chemical Catalog Co., Inc., New York, N. Y., 1927).

[8] Standard definitions of terms relating to glass and glass products, ASTM Designation: C162–52.

[9] B. C. Schmid, A. N. Finn, and J. C. Young, Thermal expansions of some soda-lime-silica glasses as functions of the composition, BS J. Research **12**, 421–28 (1934) RP667.

[10] Kuan-Han-Sun and Alexander Silverman, Additive factors for calculating the coefficient of thermal expansion of glass from its composition, Glass Industry **22**, 114–15, 125 (1941).

[11] W. E. S. Turner and F. Winks, The thermal expansion of glass. I. The general forms of the expansion curve, J. Soc. Glass Tech. **14**, 84–109T (1930).

[12] A. Dietzel and H. A. Sheybany, Problems relatifs au remplissage des vides structuraux du verre: recherches relatives aux verres alcalino-siliceux simples, Verres et Refractaires **2**, 63–80 (1948).

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