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Properties of Glasses in Some Ternary Systems Containing BaO and SiO^{*}

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The glass forming regions in six ternary oxide systems containing BaO, SiO_2 , and a third oxide have been determined. The properties of the resulting glasses were measured and the results reported. The data on refractive indices, dispersions, and specific volumes were evaluated by computer methods in an attempt to identify "substructures" containing the cations present in the glasses.

Key words: Barium glasses; barium silicates; glass properties; glass property factors; oxide glasses; silicate substructures; ternary glasses.

1. Introduction

During the course of several years, while working on the development of special purpose oxide glasses for various applications, surveys of the regions of glass formation in some ternary systems containing BaO and SiO₂ have been made. The systems surveyed are as follows:

1. BaO-TiO₂-SiO₂

- 2. $BaO-La_2O_3-SiO_2$
- 3. BaO-Ta₂O₅-SiO₂ 4. BaO-ZnO-SiO₂
- 5. $BaO-Nb_2O_5-SiO_2$
- 6. $BaO-Al_2O_3-SiO_2$

It was believed that the properties measured on the glasses are of sufficient interest to glass technologists to be made generally available and are published here.

2. Experimental Procedure

The experimental glasses were normally made in 500 g melts from batch materials of sufficient purity to satisfy the requirements for the production of optical glass. The standard procedure was to melt the batches in platinum crucibles, 6.5 cm in diameter by 7.5 cm deep. After the batch was melted, the melt was stirred for 2 h with a motor driven platinum-10-percent-rhodium, double-bladed propeller-type stirrer. The furnace used for melting was heated by silicon carbide resistance elements so that the furnace atmosphere was not contaminated by combustion products. After the melt was stirred, it was poured into a heated metal mold to form a block about 7.5 cm by 7.5 cm by 2.0 cm thick. When sufficiently rigid, the glass block was transferred to an electric muffle furnace, which was cooled to room temperature in approximately 18 h.

Only those compositions that could be melted below 1500 °C and in which no appreciable devitrification occurred during cooling were considered to produce glasses. These experimental conditions were used to define the regions of glass formation in the ternary systems studied, and no attempt was made to enlarge these regions by melting at a higher temperature or by cooling the melts more rapidly to avoid devitrification.

The properties determined for most of the experimental glasses included the following:

- (1) Sag Point [1]¹
- (2) Refractive index for the C (λ=0.6563 μm), D (λ=0.5893 μm), and F (λ=0.4861 μm) spectral lines. From these the reciprocal dispersive power, commonly known as the Nu value, ν, was calculated.

$$\nu = \frac{n_D - 1}{n_F - n_C}$$

- (3) Liquidus temperature [2]
- (4) Infrared transmittances for 2 mm thickness from 1 to 6 μ m.

For the more promising glasses certain other properties were measured. These included infrared transmittances for greater thicknesses, usually 8 mm, so that absorption coefficients could be computed; infrared refractive indices; linear coefficient of thermal expansion; and deformation temperature. For some glasses density, chemical durability, and elastic constants were also measured.

In addition, data on refractive indices (n_D) , dispersions and specific volume were evaluated, using previously described methods [3]. One purpose of this evaluation is to develop quantitative property-composition relations for use by technologists in formulating glasses for optical uses. A further purpose is to clarify presently incomplete knowledge of the ternary phase diagrams of these glass-forming systems and to identify, if possible, "substructures" containing the cations present in the glasses.

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¹ The figures in brackets indicate the literature references at the end of the paper.

3. Glass-Forming Systems Investigated

Several ternary silicate systems were investigated as to the extent of the region of glass formation and the properties of the glasses obtained.

3.1. The BaO-TiO₂-SiO₂ System

In an effort to produce glasses having high values of refractive index at wavelengths of 2.0 to 2.5 μ m, good infrared transmittances and good chemical durability melts were made in the ternary system BaO-TiO₂-SiO₂ [4]. Most high-index glasses presently available are either extra-dense flint glasses, which have a high PbO content, or rare-earth borate glasses [5]. The extra-dense flint glasses have fairly good infrared transmittances, cutting off, as do most silicate glasses, at about 5 μ m. They have high refractive indices, but their chemical durability is rather poor and they have low deformation temperatures. The B₂O₃ content of most rareearth glasses makes them useless for infrared applications.

The phase equilibrium diagram for the ternary system BaO-TiO₂-SiO₂ has not been determined, but information is available on the binary sides of the ternary system [6, 7, 8]. Rase and Roy have determined the liquidus temperatures and phase relations along the line $BaO \cdot TiO_2 \cdot SiO_2$ in the ternary diagram [9]. This information was very useful in selecting compositions in the ternary system that could be melted and cooled as glasses.

The composition of all melts made in the ternary system are given in table 1 and are plotted in the ternary diagram in figure 1. As may be seen from the figure, the longest BaO isopleth along which glasses were formed is the 25 mol percent line. Although glasses are not formed on this line to the BaO-SiO₂ binary, glass formation begins at about the 20 mol percent of TiO₂ and extends to relatively high concentrations of TiO₂. This line of glass formation seems to follow a valley in the liquidus surface, as may be seen from table 1.

The color of the glasses changed very markedly as the TiO₂ content was increased. Those containing up to about 15 mol percent of TiO₂ were nearly colorless, whereas those containing intermediate amounts from 20 to 35 mol percent of TiO₂, were orange colored, and the others having about 40 mol percent of TiO₂ were dark brown to black. Evidently, as the TiO₂ content is increased, the absorption increases at the shorter wavelengths in the visible region, and at higher TiO₂ concentrations very little visible light is transmitted.



FIGURE 1. Compositions studied in the system BaO-TiO₂-SiO₂.

| | Romorico | Nemarks | Devit in mold. Do. Do. Do. Do. Do. Do. Do. Do. Do. Some devit. Considerable | devit. Do. Do. Do. Do. Do. Do. Do. Do. Dark brown glass. Do. Black glass. Considerable | aevit. Do. Considerable | Do. Blass. Do. | Do. Do. | Do. Do. | Some devit. in end of block. |
|---------------|-------------|--|---|--|-------------------------------|----------------------|--------------------|--------------------|---------------------------------|
| | Coef. | thermal exp. | | | | 9.2×10^{-6} | - 01 × 6.9 * | 10° | 2 DT |
| | Sag | Ĵ.Ĵ | | 860 850 835 835 835 835 835 835 835 835 835 835 | | 820 820 | 815 815 | 815 820 | 820 |
| | Liquidus | °C °C | $\begin{array}{c c} 1468 \\ 1484 \\ 1484 \\ 1464 \\ 1464 \\ 1446 \\ > 1447 \\ > 1440 \\ > 1440 \\ > 1440 \\ > 1440 \\ > 1248 \end{array}$ | 1408 1345 1265 1265 1248 1233 1248 1248 1242 1260 1305 1305 | 1333 1266 | 1288 1356 1301 | $1330 \\ 1342$ | 1344 1350 | 1337 |
| ıpositions | Density | Density P | | 3.699 3.804 3.954 | | 3.743 | 3.859 3.945 | $4.004 \\ 4.079$ | 4.159 |
| 2-SiO2 con | = | 2 | | 34.0 30.6 27.6 25.3 | | 49.9 43.7 | 38.6 34.3 | 30.9 28.1 | 25.8 |
| rnary BaO-TiO | 2 | ηι | | 1.74562 1.79589 1.84382 1.89161 | | 1.64037 1.68347 | 1.72596 1.76986 | 1.81434 1.85847 | 1.90465 |
| TABLE 1. Te | 2 | (II) | | $\begin{array}{c} 1.73021\\ 1.77760\\ 1.82236\\ 1.86682\\ \end{array}$ | | 1.63139 1.67250 | 1.71276 1.75412 | 1.79585 1.83697 | 1.87998 |
| | 2 | иc | | 1.72414 1.77046 1.81406 1.85733 | | 1.62772 1.66807 | 1.70750 1.74790 | 1.78860 1.82865 | 1.87050 |
| | | ${ m TiO_2^2}$ Mol % | 202225554623252555 2225554623252555 252555 | 20115 2022 2025 2025 2025 2025 2025 2025 | 55 45 | 35 5 10 | 15 20 | 25 30 | 35 |
| | Composition | BaO Mol % | 5222 5222 5222 5222 5222 5252 5252 525 | <u> </u> | 25 27.5 | 27.5 30 30 | $30 \\ 30$ | $30 \\ 30$ | 30 |
| | | ${\mathop{\rm SiO}_2}{\mathop{\rm Mol}}$ | 855 855 855 855 855 855 855 855 855 855 | 223334455 05365 3 | 20 27.5 | 37.5 65 60 | 55 50 | 45 40 | 35 |
| | Male | No. | F294 F293 F291 F291 F300 F3316 F331 F333 F363 F363 F363 F365 | F151 F150 F149 F147 F147 F146 F145 F145 F317 F317 F333 F317 F367 | F336 F366 | F368 F152 F 35 | F 49 F 40 | F 95 F138 | F139 |

TABLE 1. Ternary BaO-TiO2-SiO2 compositions - Continued

| Bomoero | Nemarks | Some devit. Considerable | Do. | Devit. in mold. | Glass. Do. | Do. | Considerable devit. | Do. Devit in mold | Do. | Cloudy. | Some devit. | Considerable devit. | Devit. in mold. | Do. | D0. | Devit. in mola. | D0. | Do. |
|------------|---------------------------|-----------------------------|--------------|-----------------|--------------------|--------------|------------------------|----------------------|---------------|---------|-------------|------------------------|-----------------|------|------|-----------------|----------------|------|
| Coef. | or thermal exp. | | | | | | | | | | | | | | | | | |
| Sag | D°C °C | | | | 860 860 | 840 | 835 | | | | | | | | | | | |
| Liquidus | cC °C | $1354 \\ 1313$ | 1331 1302 | 1405 | 1367 | 1393 | 1415 | 1420 | 1423 1441 | 1375 | 1401 | 1441 | 1462 | 1468 | 1484 | 1404 | 1462 | 1402 |
| U | Density P | | | | 3.634 3.968 | 4.047 | | | | | | | | | | | | |
| - | 2 | | | | 49.4 | 38.3 | | | | | | | | - | | | | |
| 2 | dη | | | | 1.64310 1.70306 | 1.74401 | | | | | | | | | | | | |
| | <i>QN</i> | | | 4 | 1.63399 1 69148 | 1.73037 | | | | | | | | | | | ` | |
| | ИС | | | | 1.63026 1.68703 | 1.72494 | | | | | | | | | | | | |
| 1 | TiO Mol % | 35 40 | 45 50 | 33.3 | 2 01 | 12 | 20 | 25 | 2.8 | ь го | 10 | c۱ | 20 | 35 | 0, 1 | 0 5 | | 20 |
| Compositio | BaO Mol % | 30 30 | 30 30 | 33.3 | 35 | 35 | 35 | 35 | ç, ç, | 40 | 40 | 04 | 40 | 40 | 04 | 0 U | 0 U | 45 |
| | SiO ₂ Mol % | 35 30 | 25 20 | 33.3 | 0 22 | 2 <u>0</u> 2 | 45 | 40 | 6 8 8 | 55 | 20 | C4 | 40 | 35 | 0,5 | 00 4 | 0 1 | 35 |
| Male | No. | F288 F290 | F334 F335 | F353 | F144 F143 | F142 | F141 | F140 | F 313 F287 | F282 | F283 | F 284 | F295 | F285 | F280 | F 290 | F 29/ | F299 |

The liquidus temperature [2] for each composition is given in table 1. It will be noticed from the table that in no case was a glass formed from a composition that had a liquidus temperature greater that 1400 °C. The lowest liquidus temperatures were found along the 25 mol percent BaO isopleth, which is also the longest line of glass formation in the system. Furthermore, the shape of the liquidus curve of the 25 mol percent BaO series in the areas of best glass formation is relatively flat, indicating a high degree of dissociation of the primary phase at the liquidus temperature. Probably, the ease of glass formation is related to the degree of dissociation of the primary phase in the melt, because similar observations have been made for this and other glass forming systems [10]. In the BaO-B2O3-SiO2 system, the glasses whose compositions lie in the $3BaO \cdot 3B_2O_3 \cdot 2SiO_2$ primary field, which has a flat liquidus curve, were the ones that were melted and homogenized with the least difficulty and had the least tendency to devitrify.

The refractive index, $n_{\mathcal{P}}$, and ν are plotted in figure 2 for the three BaO isopleths along which glasses were obtained. The values of $n_{\mathcal{P}}$ varied from 1.63139 to 1.87988, and ν from 49.9 to 25.3. The refractive index appears to be a linear function of composition. The plots of ν definitely show curvature.

Figures 3 to 9, inclusive, give the transmittances for 2-mm thicknesses of the ternary glasses over the spectral range 1 to 5 μ m. The figures compare glasses of constant TiO₂ content. In general the glasses giving the highest transmittance at 4 μ m lie on the 30-mol percent BaO isopleth up to a TiO₂ concentration of 25 mol percent, then the compositions shift to the 25-mol-percent BaO isopleth. There are considerable differences in the transmittances of the various glasses, but no simple relationship between transmittance and composition is readily evident.

The values of chemical durability [11] of five representative ternary glasses are given in table 2



FIGURE 2. Plot of refractive index and ν as a function of composition for the glass-forming compositions in the BaO-TiO₂-SiO₂ system.



FIGURE 3. Spectral transmittance of 2-mm thickness of two glasses containing 5 mol percent of TiO₂. ●F152,×F144.



FIGURE 4. Spectral transmittance of 2-mm thickness of two glasses containing 10 mol percent of TiO₂. ●F35,×F143.



FIGURE 5. Spectral transmittance of 2-mm thickness of three glasses containing 15 mol percent of TiO₂.●F149, ○F142, ×F49.



FIGURE 6. Spectral transmittance of 2-mm thickness of two glasses containing 20 mol percent of TiO₂.● F148,× F40.



FIGURE 7. Spectral transmittance of 2-mm thickness of two glasses containing 25 mol percent of TiO₂. ● F147,×F95.



FIGURE 8. Spectral transmittance of 2-mm thickness of two glasses containing 30 mol percent of TiO₂. \bullet F146,×F138.



FIGURE 9. Spectral transmittance of 2-mm thickness of two glasses containing 35 mol percent of TiO₂. •F145,×F139.

and are plotted as a function of pH in figure 10. All values are for 6 h of exposure at 80 °C. As may be seen from the figure, the glass containing 60 mol percent of SiO₂ is attacked in the alkaline range. As SiO₂ is replaced by TiO₂, the attack in this range is decreased, and although slight attack or swelling is noticed at pH 2, the glasses containing 20 mol percent and more of TiO₂ show no attack in the alkaline range.

The hygroscopicity [12], or the tendency of a powdered-glass sample to absorb water in a humid atmosphere, was very low for the samples of the ternary glasses on which determinations were made. The values obtained were, in all cases, equal or less than fused silica which was used for purposes of comparison. These data are given in table 2 and plotted in figure 11.

The resistance of these glasses to chemical attack and their low hygroscopicity make them unique as compared to known oxide glasses.

The linear coefficient of thermal expansion [13] has been determined for only three representative ternary glasses. The values obtained were 9 or 10×10^{-6} /°C, which is near the values of most commercial soda-lime-silica glasses. The deformation temperatures are somewhat higher than the usual values for silicate glasses. The expansion curves for three glasses are plotted in figure 12.



FIGURE 10. Chemical durability of five BaO-TiO₂-SiO₂ glasses as a function of pH.

| TABLE | 2. | Hygroscopicity | and | chemical | durability | of | BaO- |
|-------|----|----------------|--------|-----------|------------|----|------|
| | | TiO | 2-SiO2 | 2 glasses | | | |

| M | Wa sorl | ter bed | Surfa | ice alte (expo | eration, sures, 6 | ^a fring b h at | ges, at 80 °C) | pH— |
|---------------------------|--------------------|--------------------|--------|-------------------|----------------------|------------------------------|-------------------|--------------------|
| Melt | 1 h | 2 h | 2.0 | 4.1 | 6.0 | 8.2 | 10.2 | 11.88 |
| | mg/cm ³ | mg/cm ³ | | | | | | |
| F35 | 5.7 | 10.0 | ND | ND | ND | ND | 1/2 A | 2 A |
| F49 | 6.1 | 9.1 | ND | ND | ND | ND | ND | 2/10 A |
| F40 | 5.2 | 8.2 | 1/10 A | ND | ND | ND | ND | ND |
| F95 | | | 2/10 S | ND | ND | ND | ND | ND |
| F138 | | | 1/10 S | ND | ND | ND | ND | ND |
| Corning 7740 | 15.9 | 28.3 | ND | ND | ND | DA | 1/4 A | , 1 3 A |
| Fused SiO ₂ | 6.2 | 12.1 | ND | ND | ND | ND | DA | 1/2 A |

^a ND, No detectable attack; A, attack of surface; S, swelling of surface; DA, detectable, but not measurable attack.

The deformation temperatures varied from 767 °C for glass F35, containing 10 mol percent of TiO₂, to 791 °C for glass F138, having 30 mol percent of TiO₂. The high deformation temperatures of these glasses make them unique as compared to most commercial glasses. Other data given in table 1 are the densities of several of the glasses as well as their sag points.



FIGURE 11. Hygroscopicity of three BaO-TiO₂-SiO₂ glasses compared with Corning 7740 glass and fused SiO₂.



FIGURE 12. Thermal expansion curves of three BaO-TiO₂-SiO₂ glasses as determined by an interferometric method.

3.2. The BaO-La₂O₃-SiO₂ System

Lanthanum oxide is used in optical glasses to produce relatively high values of refractive index with little or no increase in the dispersion values in the visible region. A survey of the glass forming region of the ternary system BaO-La₂O₃-SiO₂ was made. No data on the liquidus temperatures in the system were available except those in the binary BaO-SiO₂ system [8] which forms one side of the



FIGURE 13. Compositions studied in the system BaO-La₂O₃-SiO₂.

ternary system. Since then a tentative diagram for the BaO-La₂O₃ system [14] has been published. A eutectic point at about 1370 °C near the composition 30 mol percent BaO-70 mol percent SiO₂ served as a starting point.

The region of glass formation is shown in the triangular diagram in figure 13. Glasses were formed to the 12 mol percent La_2O_3 isopleth. While these compositions appear to contain rather small amounts of La_2O_3 , it must be remembered that on a weight percent basis the La_2O_3 content amounts to about 35 percent. The compositions melted and the properties of the resulting glasses are listed in table 3.

The refractive index, n_D , varied from 1.6097 to 1.7027 with ν from 56.0 to 50.8. The densities of the glasses ranged from 3.623 to 4.169 g/cm³, and the coefficient of thermal expansion ranged from 8.4 to 11.4×10^{-6} /°C.

The coefficients of thermal expansion of the glasses are plotted as a function of the composition in figure 14. The plots show an anomolous behavior



FIGURE 14. Plot of linear coefficients of thermal expansion as a function of composition for glasses in the BaO-La₂O₃-SiO₂ system.

| | A | nemarks | Opal glass. Onel in center of block | Clear glass. | Do. | Do. | Do. | Opal glass. | Clear glass. | Do. | Do. | Do. | Do. | Do. Contains some devit | | Opal glass. | Do. | Do. | Do. | Devitrified. | Clear glass. | Do. | Do. Contains some devit. | Devitrified. | Contains some devit. | Devirinea. | Contains some devit. Clear glass. |
|-------------|-------------|--|--|--------------|---------|----------------------|---------|-------------|--------------|------------|----------------|----------|---------|----------------------------|-------|--------------|---------|---------|---------|--------------|--------------|---------------|-----------------------------|--------------|----------------------|------------------|--------------------------------------|
| | Liquidus | °C. | > 1426 1 3 3 8 | 1355 | 1351 | 1373 | 1388 | > 1424 | 1213 | 1256 | 1975 | 1305 | 1307 | 1322 1340 | A 101 | 1410 | 1246 | 1335 | 1398 | 1402 1422 | > 1421 | > 1427 | 1398 1404 | > 1431 | > 1424 | > 1421 > 1421 | > 1424 > 1424 |
| | Deformation | Domination of the second secon | | 747 | c t | 742 | 755 | | 775 | L T | e// | 775 | | 775 | - | 703 | 2 | 792 | 794 | 191 | | t | /18 | | | | |
| npositions | Expansion | × 10° | | 8.9 | ~~~ | 10.0 | 10.4 | | 8.4 | , c | 4.4 | 10.8 | | 11.4 | 0.01 | ЯŔ | 0 | 9.8 | 11.3 | 6.01 | | c c | 9.3 | | | | |
| 03-SiO2 cor | Sag | °C | 781 | 108 | 202 | 06/ | 262 | | 000 | 798 | 708 | 810 | 810 | 810 835 | 000 | 848 | 835 | 840 | 835 | 048 | 862 | 850 | 808 098 | | 880 | | 855 |
| ry BaO-La2(| | ρ | | 3.623 | 0.00 | 3.819 | 3.997 | | 3.663 | 3.768 | 3.000 3.064 | 4.076 | 4.132 | 4.243 | | 3 840 | 3.923 | 4.121 | 4.276 | 4.38/ | | 4.085 | 4.109 | | | | |
| Terna | ; | 2 | | 56.0 | 55.6 | 54.9 54.3 | 53.8 | | 55.4 | 54.8 | 7.40 | 53.3 | 52.6 | 51.9 | | 54.9 | 53.8 | 52.6 | 51.5 | 8.06 | 52.3 | 52.7 | 0.26 | | 50.8 | | 50.8 |
| TABLE 3. | 1 | μĿ | | 1.61743 | 1.62465 | 1.63662 1 64608 | 1.65462 | | 1.62864 | 1.63978 | feren.t | 1.67007 | 1.67598 | 1.68584 | | 1 65970 | 1.66086 | 1.68057 | 1.69530 | 1./040/ | 1.67942 | 1.68352 | 7/160.1 | | 1.71255 | | 1.70927 |
| | | d n | - | 1.60974 | 1.61685 | 1.62855 | 1.64611 | | 1.62076 | 1.63162 | 1.04299 | 1.66126 | 1.66700 | 1.67660 | | 1 64498 | 1.65227 | 1.67152 | 1.68584 | 1.04490 | 1.67032 | 1.67445 | 1.08243 | | 1.70275 | | 1.69950 |
| | 1 | Ju | | 1.60655 | 1.61357 | 162591 | 1.64261 | | 1.61743 | 1.62824 | Striated | 1.65768 | 1.66330 | 1.67280 | | 1 64081 | 1.64872 | 1.66779 | 1.68199 | 1.09UW | 1.66660 | 1.67071 | 100/0.1 | | 1.69872 | | 1.69550 |
| | | ${ m SiO}_2$ Mol % | 75 73 | 20 | 89 | 60 63 | 30 | 75 | 72 | 02 | 29 | 62 | 60 | 8 8 | 3 | 73 | 89 | 63 | | 6 <u>6</u> | 70 | 67 | 62 03 | 60 | 28 7 8 | 22.5 | 68 65 |
| | mpositior | La2O3 Mol % | 0 10 | 101 | 00 | n c | 101 | 5 | ы С | ر ت ا | о .c | <u>م</u> | 5 2 | <u>م</u> م | > | ~ ~ | . ~ | 2 | - 1 | - 1- | 10 | 10 | 10 | 10 | 010 | 10 | 12 12 |
| | Co | BaO Mol % | 23 | 38 | 30 | 20 20 20 20 | , œ | 20 | 23 | <u>6</u> 2 | 308 | 33 | 35 | 37 | | 20 | 25 | 30 | 35 | 40 | 20 | 23 | 78 79 | 30 | 32 35 | 37 | 20 23 |
| | Male | No. | F547 F548 | F518 | F634 | F558 | F561 | F550 | F551 | F530 | F525 | F563 | F527 | F564 F528 | | F562 F552 | F538 | F530 | F539 | F560 | F627 | F554 Ec.4c | F555 | F526 | F631 F639 | F633 | F629 F628 |



FIGURE 15. Spectral transmittance of 2-mm thickness of glasses containing 2 mol percent of La₂O₃. ● F558, ○F548, × F634.

for the 5 and 7 mol percent La₂O₃ lines, and it is possible that the 2 mol percent line would show a similar behavior if data were obtained at higher BaO concentrations. The increase in the values of coefficient of expansion with increasing amounts of BaO, and decreasing SiO₂ content, is not surprising. But the curve reaches a maximum and then decreases as the SiO₂ content continues to decrease. An explanation for this behavior is not readily apparent.

At the same time, for each La_2O_3 isopleth, there is little change in deformation temperature, so that it does not appear that the increase in the coefficient of expansion is due solely to a loosening of the structure as more BaO is incorporated into the glass. As shown in the table the deformation temperatures of the glasses vary little within each series, but definitely increase as the La_2O_3 content of the glasses increases.

The transmittance curves for 2-mm thicknesses of glasses in the 2, 5, 7, and 10 mol percent La₂O₃ series are plotted in figures 15, 16, 17, and 18. The curves are plotted from the limit of transmittance in the ultraviolet to 0.5 μ m and from 2.0 μ m to the limit of transmittance in the infrared. While transmittance values have not been measured from 0.5 to 1.0 μ m, there is no reason to expect any change in transmittance in this region because the glasses are clear and show no evidence of absorption. The ultraviolet limit of transmittance, about 0.260 μ m, is somewhat beyond the usual run of glasses. Window glass, for instance, does not transmit beyond about 0.320 μ m in 2.0 mm thicknesses. thicknesses. In the infrared there are variations in



FIGURE 16. Spectral transmittance of 2-mm thickness of glasses containing 5 mol percent of La₂O₃. \bullet F525, \times F551, - F527.

the transmittance curves between 3 and 4 μ m, but no simple relation with composition is readily evident.

3.3. The BaO-Ta₂O₅-SiO₂ System

Tantalum oxide, used as a component of glass, imparts higher refractive index values and higher dispersions than does La_2O_3 . A survey of the glassforming region of the BaO-Ta₂O₅-SiO₂ ternary system was made. Again no data were found on the liquidus temperatures in the systems except for the BaO-SiO₂ binary system [8]. The eutectic point in the binary system at about 1370 °C served again as a starting composition.



FIGURE 17. Spectral transmittance of 2-mm thickness of glasses containing 7 mol percent of La₂O₃. \bullet F552, \times F530, - F553.



FIGURE 18. Spectral transmittance of 2-mm thickness of glasses containing 10 mol percent of La₂O₃. ● F554, × F545, ○F555.

The region of glass formation is shown in the triangular diagram in figure 19. The compositions melted and the properties of the glasses are given in table 4. The glasses form series along the 2, 5, 7, and 10 mol percent Ta₂O₅ isopleths as may be seen from the figure. The refractive index, n_D , varied from 1.6112 to 1.7708 with ν from 53.5 to 39.4. The densities of the glasses ranged from 3.672 to 5.015 g/cm³. The coefficients of thermal expansion were determined for only two glasses, one in the 5 mol percent and one in the 10-mol-percent Ta₂O₅

series. The values were 8.3×10^{-6} and 9.5×10^{-6} °C respectively. The deformation points for the two glasses were 800 and 853 °C, which are rather high compared to those of most silicate glasses.

The transmittances from the limit of transmittance in the ultraviolet to 0.500 μ m, and from 2 μ m to the limit of transmittance in the infrared for 2-mm thicknesses of glasses from the 2, 5, 7, and 10 mol percent series are given in figures 20, 21, 22, 23, and 24.

| Remarke | | Opal glass. Do. Do. Do. Do. Do. Do. Do. Do. Do. Do | Slight devitrification. Clear glass. Do. |
|-------------|---|---|---|
| Liquidus | °C | > 1414 1335 1355 1356 1376 1371 1403 1390 1390 1390 1390 1325 1325 1325 1325 1325 1325 1325 1325 | > 1431 > 1425 > 1425 |
| Deformation | °C | 800 | 853 |
| Expansion | × 106 | 8.3 | 9.5 |
| Sag | °C | 835 835 835 835 835 835 840 855 855 855 855 855 855 855 855 855 85 | 880 880 |
| Dansity | p | 3.672 3.672 3.770 3.929 4.005 4.151 4.151 4.192 4.140 4.481 4.418 4.418 4.418 4.480 4.481 4.676 4.480 4.696 4.696 4.771 4.771 4.771 | 5.015 |
| ; | 4 | 53.5 53.5 53.5 53.2 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.3 55.4 48.4 45.4 45.4 45.4 45.4 44.4 44.4 44.4 44.4 44.4 44.4 | $39.4 \\ 42.2 \\ 41.0$ |
| 1 | чĿ | $\begin{array}{c} 1.61928\\ 1.62972\\ 1.65237\\ 1.65237\\ 1.65237\\ 1.67037\\ 1.67037\\ 1.67037\\ 1.68966\\ 1.68966\\ 1.68972\\ 1.689242\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72431\\ 1.72336\\ 1.72330\\ 1.75380\\ 1.7580\\ 1.75380\\ 1.758$ | 1.76153 1.76564 1.78424 |
| ŝ | a an | $\begin{array}{c} 1.61119\\ 1.62145\\ 1.63706\\ 1.64360\\ 1.64325\\ 1.66117\\ 1.66117\\ 1.66117\\ 1.66759\\ 1.6759\\ 1.67759\\ 1.67759\\ 1.67759\\ 1.71249\\ 1.71249\\ 1.71249\\ 1.71249\\ 1.71249\\ 1.712624\\ 1.712624\\ 1.712624\\ 1.72595\\ 1.72595\\ 1.72595\\ 1.771844\\ 1.72595\\ 1.771844\\ 1.72595\\ 1.771844\\ 1.72595\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.771844\\ 1.772545\\ 1.771844\\ 1.77$ | $\begin{array}{c} 1.74766\\ 1.75293\\ 1.77082\end{array}$ |
| 5 | <i></i> | 1.60786 1.60786 1.63352 1.653998 1.653942 1.65740 1.65740 1.65744 1.65744 1.65744 1.65744 1.65744 1.65744 1.65744 1.65744 1.65745 1.70802 1.70802 1.70870 1.70876 1.70877 1.70876 1.70877 1.70876 1.770876 1.7708776 1.77087777777777777777777777777777777777 | 1.74254 1.74781 1.76542 |
| q | SiO ₂ Mol % | 73 665 665 665 660 668 668 668 668 668 668 668 668 668 | 50 45 42 |
| ompositio | Ta ₂ O ₅ Mol % | | 10 10 10 |
| Ŭ | BaO Mol % | 25 23 <th23< th=""> 23 23 23<!--</td--><td>40 45 48</td></th23<> | 40 45 48 |
| Melt | No. | 7575 7522 7531 7576 7577 7577 7579 7579 7588 7540 7540 7534 7591 7591 7591 7591 7591 7591 7591 7591 | 7593 6616 6617 |

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TABLE 4. Ternary BaO-Ta2Os-SiO2 compositions



FIGURE 19. Compositions studied in the system BaO-Ta₂O₅-SiO₂.

3.4. The BaO-ZnO-SiO₂ System

ZnO may be used as a component of glass. It imparts intermediate values of refractive index and some glasses containing ZnO have relatively low values of thermal expansion. A survey of the glassforming region of the BaO-ZnO-SiO₂ system was made. Data on the binary $BaO-SiO_2$ [8] and the $ZnO-SiO_2$ [15] systems are available.

The region of glass formation found in the system is shown in the triangular diagram in figure 25, and the compositions melted are listed in table 5. As may be seen from the figure clear glasses were obtained over a considerable area of the diagram.

The liquidus temperatures of the various compositions are also given in table 5. The glasses, over a relatively large composition area, have liquidus temperatures below 1300 °C. A smaller area has liquidus temperatures below 1200 °C and a still smaller area has temperatures below 1100 °C. The minimum liquidus temperature found was 1089 °C for a glass on the 26-mol-percent BaO isopleth.

The refractive index values for glasses in the system are also given in the table. The values range from 1.5878 to 1.6785 for n_D with ν from 48.4 to 56.8.

The transmittance curves for 2-mm thicknesses of glasses from the 36, 30, 26, 20, 14, and 10 mol percent BaO series are given in figures 26, 27, 28, 29, 30, and 31, respectively. For each series there is considerable spread in the transmittance values for the region between 2.75 to 4.0 μ m as the SiO₂ content is varied. If one examines the transmittance values at 3.5 μ m as the BaO content is decreased, it appears that the trend is for a decrease in transmittance from the 36 to the 30 mol percent series. Then the trend is for a gradual increase from the 30 to the 10 mol percent series. It would appear from the general shapes of the curves that some of the variations are due to the (OH)⁻ content of the glasses.



FIGURE 20. Spectral transmittance of 2-mm thickness of glasses containing 2 mol percent of Ta₂O₅. ● F522, × F588, ○ F576.



FIGURE 21. Spectral transmittance of 2-mm thickness of glasses containing 5 mol percent of Ta_2O_5 . \bullet F532, \times F534, Δ F542.



FIGURE 22. Spectral transmittance of 2-mm thickness of glasses containing 5 mol percent of Ta₂O₅. ● F579. × F580. ○ F540.



FIGURE 23. Spectral transmittance of 2-mm thickness of glasses containing 7 mol percent of Ta₂O₅. ●F584, × F615, ○F591.



FIGURE 24. Spectral transmittance of 2-mm thickness of glasses containing 10 mol percent of Ta₂O₅. ●F616, ○F617.

| Remarks | | Some devit. Some devit. Clear glass. Devit in mold. | Some devit. | Some devit. | Clear glass. Clear glass. Clear glass. Clear glass. Devit in mold. Did not melt. | Some devit. | Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Some devit. | Clear glass. | Clear glass. Clear glass. Devit in mold. | Slight devit. Slight devit. Clear glass. |
|---------------------|---------------------------|--|-------------|-------------|---|-------------|---|--------------|--|--|
| Coef. of Thermal | $\exp \times 10^6$ | | | | 10.5 | | | | | |
| Sag Point | ٦° | 810 800 800 | 766 | 785 | 800 765 748 748 | 786 | 728 | 795 | 728 | 764 764 764 |
| Liquidus | Temp. °C | 1345 1304 1288 1387 | 1407 | 1395 | 1341 1268 1212 1281 > 1414 | 1400 | 1329 1277 1193 1167 1229 1315 | 1374 | 1172 1152 1405 | 1400 1385 1350 |
| = | 2 | 49.7 | | | 53.8 52.1 50.8 49.6 | | 52.8 51.7 51.1 50.3 50.0 | 55.5 | 51.4 50.9 | |
| 1 | An | 1.68817 | | | 1.64406 1.66261 1.67474 1.68574 | | $\begin{array}{c} 1.65327\\ 1.65222\\ 1.67112\\ 1.67841\\ 1.67968\\ 1.67968\end{array}$ | 1.61862 | 1.66504 1.67151 | |
| | <i>an</i> | 1.67848 | | | 1.63568 1.65371 1.6544 1.67605 | | 1.64461 1.65327 1.66192 1.66898 1.67017 | 1.61084 | 1.65598 1.66228 | |
| | μC | 1.67453 | | | 1.63224 1.65006 1.66165 1.67210 | | 1.64106 1.64960 1.65815 1.65815 1.66512 1.66629 | 1.60761 | 1.65227 1.65849 | |
| | SiO ₂ Mol % | 54 50 46 42 | 58 | 60 | 58 54 50 38 38 38 | 62 | 560 57 57 50 54 50 54 50 54 | 64 | 52 50 42 | 20 99 90 |
| Composition | ZnO Mol % | 6 10 14 18 | ŝ | 3 | 6 10 18 22 26 22 | ę | 6 114 22 22 22 | 3 | 16 18 26 | 04 |
| | BaO Mol % | 40 40 40 40 | 39 | 37 | **** | 35 | 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 | 33 | 32 32 32 | 30 30 30 |
| | Melt | F829 F830 F831 F831 F832 | F850 | F847 | F828 F786 F787 F788 F833 F833 | F848 | F783 F760 F761 F764 F762 F762 F785 | F849 | F784 F766 F835 | F690 F691 F692 |

| | Remarke | MCIII 01 NS | Clear glass. Clear glass. | Clear glass. | Clear glass. | Clear glass. | Clear glass. | Clear glass. | Clear glass. | Devit in mold. Devit in mold. | Clear glass. | Clear glass. Striated | Clear glass. | Devit in mold. | Devit in mold. | Clear glass. | Clear glass. |
|---------------|---------------------|-----------------------|------------------------------|--------------|---------------|--------------|--------------|--------------|--------------------|----------------------------------|--------------|--------------------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|----------------|----------------|--------------|--------------|--------------|--------------|--------------|--------------|----------------|-------------------|
| | Coef. of Thermal | $exp. \times 10^6$ | | 9.2 | | | | | | | 8.6 | | | | 9.2 | | | k (| 6.6 | | | | | | | | | | |
| | Cog Doint | | 764 764 | 267 | 762 | 760 | 200 | 769 | 750 | | 692 | 760 | 269 2007 | 767 | 269 | 768 | 750 | 750 | 067 | | | 802 | 780 | e11 | 202 | 762 | 762 | 763 | 200 |
| 1s-Continued | I taniduo | Liquidus Temp. °C | 1312 1998 | 1269 | 1224 | 1193 | 1142 | 0111 | 1285 | > 1425 > 1406 | 1355 | 1335 | 1290 | 1278 | 1220 | 1181 | 1141 | 1165 | 1261 | DOCT | > 1407 | 1333 | 1315 | 1285 | 1255 | 1235 | 1199 | 1148 | 1177 |
| composition | ; | a | 55.3 | 0.40 | 04:0 7.8.5 | 52.7 | 52.0 | 51.5 | 50.8 49.6 | | 56.8 | | 6 11 | 54.6 54.6 | 53.9 | 52.8 | 52.6 | 51.4 | 50.0 | 49.2 | | | 56.6 | 56.0 | 6.66 6.73 | 54.5 | 53.6 | 53.0 | 6.26 51.7 |
| BaO-ZnO-SiO2 | | ar. | 1.62156 | 1.02980 | 1.64071 | 1.65002 | 1.65735 | 1.66330 | 1.66949 1.68316 | | 1 60134 | 101001 | 919191 | 1.01010 | 1.63360 | 1.64354 | 1.64892 | 1.66112 | 1.67672 | 1.08412 | | | 1.59672 | 1.60528 | 1 61799 | 1.62581 | 1.63164 | 1.64201 | c0/401 1.65617 |
| LE 5. Ternary | 1 | <i>u</i> _D | 1.61369 | 1 69800 | 1 63232 | 1.64141 | 1.64852 | 1.65430 | 1.60028 | | 1.59392 | | 1 61035 | 1.61880 | 1.62540 | 1.63501 | 1.64029 | 1.65212 | 1.66725 | 1.0/438 | | | 1.58933 | 1.59772 | 1,60041 | 1.61779 | 1.62336 | 1.63354 | 1.03042 |
| TAB | | л _С | 1.61047 | 140101 | 1.62890 | 1.63785 | 1.64489 | 1.65060 | 1.66957 | | 1.59088 | | 1 60711 | 1.61549 | 1.62199 | 1.63151 | 1.030/4 | 1.64842 | 1.66336 | 04010.1 | | | 1.58630 | 1.59460 | 1 60618 | 1.61447 | 1.62000 | 1.63005 | 1.64365 |
| | | SiO2 Mol % | 64 69 | 39 | 28 | 56 | 54 | 22 | 99 | 42 40 | 20 | 68 | 8 3 | 62 | 09 | 88.5 | 8 7 7 | 52 | 48 | \$ 4 | 42 | 72 | 20 | 80 99 | 64 | 62 | 09 | 8 Y | 54 |
| | Composition | ZnO Mol % | ۵۵ | ° <u>°</u> | 12 | 14 | 16 | 81 G | 24 24 | 30 30 | 2 | 4 | - ~ | 10 | 12 | 14 | <u>0</u> 81 | 20 | 24 | 3 83 | 30 | 2 | 4, | ۵۵ | 90 | 12 | 14 | 0 8 | 20 |
| | | BaO Mol % | 30 30 | 08 | 30 | 30 | 30 | 000 | 30 | 0, 0, | 28 | 38 38 | 8 8 | 88 | 58 | 88 e | 8 8 | 28 | 83 8 | 38 | 28 | 26 | 50 50 | 92 S2 | 26 26 | 26 | 26 | 8,8 | 26 |
| | Mala | MEIL | F693 F694 | F695 | F711 | F712 | F713 | F715 | F722 | F758 F767 | F696 | F699 F700 | F701 | F702 | F703 | F717 F718 | F719 | F720 | F 123 F775 | F776 | F836 | F704 | F705 | F707 | F708 | F709 | F710 | F / 10 F731 | F721 |

| | Remarks | Clear glass. Clear glass. Considerable devit. | Opal glass. Opal glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Slight devit. Some devit. Devit in mold. | Opal glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Clear glass. Some devit. | Clear glass. Clear glass. Opal glass. Slight opal. Clear glass. |
|-------------|-----------------------------------|---|--|--|---|
| Coef. of | Thermal exp. × 10 ⁶ | 9.3 | | 7.9 | 6.9 |
| | Sag Point °C | 760 755 | 768 763 763 763 763 760 750 750 743 727 | 800 763 763 763 740 740 740 727 | 755 755 755 755 |
| | Liquidus Temp. °C | 1250 1325 1316 | > 1425 1408 1327 1327 1327 1140 11102 1128 1128 1228 1228 1228 1224 1325 1327 | 1357 1217 1153 1125 1126 1126 1217 1252 1274 1283 1340 | 1276 1276 1336 1127 |
| | 2 | 50.4 49.1 | 56.6 55.5 53.0 53.0 51.0 51.0 51.0 51.0 51.0 | 54.9 53.0 50.7 50.0 50.0 | 48.9 52.7 |
| | n_F | 1.67044 1.68336 | $\begin{array}{c} 1.59519\\ 1.60990\\ 1.62426\\ 1.62472\\ 1.65473\\ 1.65473\\ 1.65017\\ 1.65157\end{array}$ | 1.61084 1.63488 1.62985 1.65849 1.66482 | 1.62604 |
| | ПD | 1.66112 1.67361 | 1.58785 1.60228 1.61622 1.64102 1.643102 1.643102 1.643102 1.66216 | 1.60307 1.62651 1.62158 1.62158 1.65553 1.65553 | 1.66436 |
| | ис | 1.65731 1.66964 | $\begin{array}{c} 1.58480\\ 1.5904\\ 1.5904\\ 1.61290\\ 1.62586\\ 1.63743\\ 1.64219\\ 1.64219\\ 1.65830\\ 1.65830\end{array}$ | 1.59986 1.62306 1.61816 1.64567 1.64567 | 1.66042 |
| | SiO2 Mol % | 50 46 44 | 72 72 72 72 72 72 72 72 72 72 72 72 72 7 | 5 4 4 8 5 5 5 4 8 9 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 54 64 60 60 |
| Composition | ZnO Mol % | 24 28 30 | 338887555588190 e + 5 33888875555 | 5 33 3 8 8 5 5 5 8 1 1 0 3 3 3 3 8 8 6 5 5 9 1 1 1 0 | 24 24 25 20 24 |
| | BaO Mol % | 26 26 26 | 22222222222222222222222222222222222222 | &&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&& | 16 16 18 18 |
| Malt | TICH | F724 F757 F789 | F725 F726 F726 F727 F730 F745 F745 F745 F754 F755 F754 F756 F756 F756 | F732 F733 F734 F763 F744 F755 F774 F774 F774 F771 F811 F803 | F806 F792 F793 F794 |

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TABLE 5. Ternary BaO-ZnO-SiO₂ compositions-Continued

н.

| | Remarks | Clear glass. Clear glass. Clear glass. Some devit. | Opal glass. Slight devit. Slight devit. | Slight devit. Clear glass. Clear glass. Clear glass. Clear glass. | Slight devit. Clear glass. Clear glass. Clear glass. Slight devit. | Slight opal. Clear glass. Clear glass. Clear glass. | Clear glass. | Opal glass. Opal glass. Clear glass. Considerable devit. | Devit in mold. Devit in mold. |
|-------------|-----------------------------------|---|---|--|--|--|--------------|---|----------------------------------|
| Coef. of | I hermal exp. $\times 10^6$ | | | | 7.2 | | 5.7 | | |
| San D | Sag Foint °C | 738 727 728 | 766 765 765 | 765 737 727 725 | 745 737 738 738 730 715 | 735 727 727 735 | 738 | 735 727 | |
| l ianiduo | Temp. °C | 1162 1205 1333 | > 1407 1257 1254 | 1283 1203 1260 1252 1326 | 1233 1245 1246 1304 1342 1402 | 1293 1307 1340 1390 | 1371 | > 1412 > 1408 1403 1403 | > 1425 > 1407 |
| | 2 | 50.5 49.5 | 53.0 | 51.4 49.9 48.5 48.0 | 51.8 51.3 50.4 49.2 47.9 | 50.1 49.4 48.4 | 48.7 | 49.0 | |
| 2 | иĿ | 1.64727 1.66454 | 1.61966 | 1.63789 1.65593 1.66906 1.67816 | 1.62989 1.63543 1.64699 1.66235 1.66847 1.67923 | $\begin{array}{c} 1.64572 \\ 1.65348 \\ 1.66776 \end{array}$ | 1.66047 | 1.65066 | |
| | (I) | 1.63832 1.65516 | 1.61148 | $\begin{array}{c} 1.62923 \\ 1.64675 \\ 1.65940 \\ 1.66826 \end{array}$ | $\begin{array}{c} 1.62139\\ 1.62677\\ 1.63803\\ 1.65292\\ 1.65882\\ 1.66930\end{array}$ | $\begin{array}{c} 1.63671 \\ 1.64424 \\ 1.65810 \end{array}$ | 1.65098 | 1.64134 | |
| | nc | 1.63462 1.65131 | 1.60812 | $\begin{array}{c} 1.62566\\ 1.64298\\ 1.65546\\ 1.65546\\ \end{array}$ | $\begin{array}{c} 1.61789\\ 1.62320\\ 1.62324\\ 1.63434\\ 1.64908\\ 1.65487\\ 1.6526\end{array}$ | $\begin{array}{c} 1.63301 \\ 1.64045 \\ 1.65416 \end{array}$ | 1.64709 | 1.63757 | |
| | ${\mathop{\rm SiO}}_2^2$ Mol $\%$ | 56 54 50 46 | 64 60 20 | 55 56 46 48 55 56 56 56 56 56 56 56 56 56 56 56 56 | 50 55 55 58 50 48 55 55 58 | 56 53 48 | 50 | 56 52 48 | 50 52 |
| Composition | ZnO Mol % | 30 28 34 33 38 | 22 24 26 | 28 34 38 40 88 | $\begin{array}{c} 32\\ 22\\ 23\\ 24\\ 23\\ 23\\ 23\\ 23\\ 23\\ 23\\ 23\\ 23\\ 23\\ 23$ | 34 36 38 38 38 | 42 | 38 42 46 | 46 44 |
| | BaO Mol % | 16 16 16 | 14 14 14 | 14 14 14 | 2222222 2222222 | 10001 | 8 | مممم | 44 |
| | Melt | F795 F808 F797 F810 | F845 F844 F838 | F837 F816 F802 F805 F839 | F841 F840 F809 F798 F842 F843 | F817 F813 F801 F804 | F799 | F818 F814 F815 F815 | F800 F846 |

i.

TABLE 5. Ternary BaO-ZnO-SiO₂ compositions-Continued



FIGURE 25. Compositions studied in the system BaO-ZnO-SiO₂.

FIGURE 26. Spectral transmittance of 2-mm thickness of glasses containing 36 mol percent of BaO. \bullet F786, Δ F787, \times F788.





FIGURE 27. Spectral transmittance of 2-mm thickness of glasses containing 30 mol percent of BaO. - F690, \bullet F692, Δ F694, \times F711.



FIGURE 28. Spectral transmittance of 2-mm thickness of glasses containing 26 mol percent of BaO. × F705, ●F707, Δ F709, - F716.









FIGURE 30. Spectral transmittance of 2-mm thickness of glasses containing 14 mol percent of BaO. ●F816, △ F802, × F805.



FIGURE 31. Spectral transmittance of 2-mm thickness of glasses containing 10 mol percent of BaO. ● F813, △ F801, × F804.

3.5. The BaO-Nb₂O₅-SiO₂ System

Nb₂O₅, when used as a component of glass, imparts relatively high values of refractive index along with high dispersion, or low ν . The glassforming region of the BaO-Nb₂O₅-SiO₂ system was determined. Information on the binary sides, BaO-SiO₂ [8], BaO-Nb₂O₅ [16], and Nb₂O₅-SiO₂ [17], is available, but the ternary system has not been worked out.

The region of glass formation in the system is shown in the triangular diagram in figure 32, and the compositions melted and their measured properties are listed in table 6. Except for the 2 and 6 mol percent glasses, most of the melts had liquidus temperatures below 1300 °C. A minimum value of 1152 °C was found for one glass in the 14-mol-percent Nb₂O₅ series. Glasses were formed to remarkably low SiO₂ contents, as may be seen from the table and from figure 32. Glass F1466 contained 38mol-percent SiO₂.

The refractive index, n_D , ranged from 1.615 to 1.902 with ν from 51.7 to 27.6.

The transmittance curves for 2 mm thicknesses of the glasses from the 2, 6, 10, 14, 18, and 22 mol percent Nb₂O₅ series are shown in figures 33 to 38, respectively. As the Nb₂O₅ content of the glasses increase the minimum in transmittance in the 2.75 to 4 μ m region increases. This evidently is related to the (OH)⁻ content of the glasses and to the manner in which (OH)⁻ is bound, but no general explanation of this behavior is readily seen.



FIGURE 32. Compositions studied in the system BaO-Nb₂O₅-SiO₂.

| | Remarks | Seedy glass. Clear glass. Do. Do. | Devit in mold. Do. Clear glass. Do. Do. Do. Devit in mold. | Devit in mold. Clear glass. Do. Do. Opal during anneal. | Devit in mold. Clear glass. Do. Do. Do. Opal on cooling. | Devit in mold. Clear glass. Clear yellowish glass. Do. Do. Opal on cooling. | Devit in mold. Clear yellowish glass. Do. Devit streaks on cooling. Do. | Devit streak & seedy. Devit streaks on cooling. |
|--|----------------------|--|---|--|--|--|--|--|
| | Lıquıdus Temp. °C | 1348 1343 1380 1394 | 1339 1331 1336 1274 | 1212 1244 1246 1226 | 1273 1250 1191 1191 1152 | 1295 1240 1247 1203 1203 | 1306 1274 1286 1262 | |
| 00 · · · · · · · · · · · · · · · · · · | Sag Foint C | 812 818 809 822 | 819 813 832 | 835 827 868 843 | 853 862 837 850 | 862 836 856 856 | 872 862 887 | 887 |
| | л | 51.7 51.1 50.5 49.6 | 43.8 43.0 42.7 40.8 | 37.9 37.7 38.1 37.6 | 33.5 33.6 33.6 33.7 33.8 | 29.8 30.2 30.5 31.0 | 27.6 27.8 | |
| | n_F | 1.62341 1.64352 1.65704 1.67345 | 1.69856 1.71558 1.72739 1.74573 | 1.75373 1.76803 1.77385 1.77884 | $\begin{array}{c} 1.80532\\ 1.81887\\ 1.83002\\ 1.83888\\ 1.83888\\ 1.84529\end{array}$ | 1.85805 1.86945 1.87702 1.88533 1.88983 | 1.91444 1.92498 | |
| | an | 1.61497 1.63471 1.64794 1.66394 | 1.68738 1.70391 1.71543 1.73290 | 1.73 <i>977</i> 1.75372 1.75959 1.77413 | 1.78844 1.80176 1.81269 1.82140 1.82777 | $\begin{array}{c} 1.83792\\ 1.84922\\ 1.85680\\ 1.86508\\ 1.86967\end{array}$ | 1.89116 1.90166 | |
| | лc | 1.61152 1.63111 1.64421 1.66006 | 1.68287 1.6921 1.71062 1.72775 | 1.73419 1.74802 1.75390 1.76825 | 1.78176 1.79500 1.80584 1.81450 1.82084 | 1.82988 1.84130 1.84890 1.85714 1.86176 | 1.88213 1.89258 | |
| | Nb2O5 Mol % | 0000 | ~~~~~~ | 0000000 | 144 144 144 144 | 18 18 18 18 18 18 18 18 18 18 | 22 22 22 22 | 26 26 |
| Compositions | BaO Mol % | 28 32 40 82 82 | 224 23 23 24 24 24 24 24 24 24 24 24 24 24 24 24 | 28 32 44 44 86 85 86 82 86 82 86 82 86 86 86 86 86 86 86 86 86 86 86 86 86 | 5284403328 5284403328 | 5 8 4 4 0 3 3 2 8 5 8 4 4 0 3 3 2 8 | 32 36 44 48 48 49 | 40 44 |
| | SiO2 Mol % | 28 58 58 58 58 58 58 58 58 59 50 50 50 50 50 50 50 50 50 50 50 50 50 | 65 55 55 55 55 55 55 55 55 55 55 55 55 5 | 55 54 55 54 56 54 56 54 56 54 50 54 50 54 50 54 50 55 54 50 55 54 55 55 54 55 55 55 55 55 55 55 55 | 55 50 50 50 54 50 55 55 55 55 55 55 55 55 55 55 55 55 | 50 50 33 34 50 50 50 50 50 50 50 50 50 50 50 50 50 | 46 332 34 334 334 30 40 334 30 30 40 50 30 30 40 50 50 50 50 50 50 50 50 50 50 50 50 50 | 34 30 |
| | Melt No. | F1431 F1432 F1433 F1433 | F1435 F1435 F1437 F1437 F1438 F1439 F1445 F1486 | F1441 F1442 F1443 F1444 F1446 F1456 | F1447 F1448 F1449 F1450 F1451 F1451 F1488 | F1458 F1459 F1461 F1461 F1462 F1463 F1489 | F1464 F1465 F1466 F1490 F1491 | F1492 F1493 |

TABLE 6. Ternary BaO-Nb2O5-SiO2 compositions



FIGURE 33. Spectral transmittance of 2-mm thickness of glasses containing 2 mol percent of Nb₂O₅. ○F1431, ●F1432, +F1433, ×F1434.



FIGURE 35. Spectral transmittance of 2-mm thickness of glasses containing 10 mol percent of Nb₂O₅. **•**F1442, **•**F1443, **+**F1444.



FIGURE 34. Spectral transmittance of 2-mm thickness of glasses containing 6 mol percent of Nb₂O₅. •F1437, •F1438, +F1439.

FIGURE 36. Spectral transmittance of 2-mm thickness of glasses containing 14 mol percent of Nb₂O₅. + F1448, \bullet F1449, \circ F1451.

100





FIGURE 37. Spectral transmittance of 2-mm thickness of glasses containing 18 mol percent of Nb₂O₅. ○F1460, + F1461, ●F1462, △ F1463.

FIGURE 38. Spectral transmittance of 2-mm thickness of glasses containing 22 mol percent of Nb₂O₅. •F1465, +F1466.



FIGURE 39. Compositions studied in the system BaO-Al₂O₃-SiO₂ and approximate phase boundaries.

| - | nemarks | Seedy. | Seedy. Do. Do. Striated. Impossible to measure index. Striated. | Seedy. Do. Striated. Striated. Striated. | Seedy. Do. Do. Striated. Striated. Striated. Striated. Striated. |
|-------------|--|--|---|--|---|
| | Dag Folm C | 857 857 840 832 832 832 832 | 874 874 853 840 838 838 838 838 838 838 838 838 | 848 830 833 833 830 830 830 850 850 857 | 833 872 879 898 898 898 898 898 898 895 |
| - | Liquidus Temp. °C | 1208 1268 1286 1277 1263 1263 | 1162 1166 1205 1177 1177 1232 1176 1247 1305 | 1332 1377 1368 1368 1368 1368 1368 1367 1347 1292 | >1404 >1411 >1411 >1425 1337 >1445 1379 |
| | 2 | 55.5 55.5 54.3 54.3 54.3 54.3 | 56.6 54.9 55.4 53.4 53.4 | 57.0 57.0 56.1 54.4 54.4 54.4 54.4 53.8 | 54.7 54.7 52.9 52.5 51.4 51.7 51.7 51.7 52.4 53.0 |
| | n_F | 1.61537 1.61991 1.62264 1.63672 1.63993 1.64415 | 1.60501 1.62827 1.63280 1.63260 1.64309 1.65063 | 1.60132 1.60132 1.60942 1.61535 1.61535 1.61535 1.63394 1.63952 1.63784 1.64523 | 1.63163 1.64501 1.64501 1.65554 1.65552 1.65552 1.66452 1.65635 1.64937 1.64937 |
| | an a | 1.60758 1.61207 1.61483 1.62862 1.63170 1.63586 | 1.59760 1.59760 1.62023 1.62473 1.62473 1.63475 1.63475 | 1.59397 1.60200 1.60770 1.61612 1.62189 1.63127 1.6364 | 1.62357 1.62357 1.63360 1.64390 1.64972 1.64972 1.64972 1.6475 1.6475 1.64765 1.64765 1.64765 1.64689 |
| | n _C | 1.60438 1.60887 1.61158 1.62514 1.62831 1.62831 | 1.59445 1.61694 1.62142 1.62491 1.63133 1.63861 | 1.59091 1.59885 1.60452 1.61284 1.61284 1.61284 1.61284 1.63339 | 1.62024 1.62024 1.63315 1.64614 1.64614 1.65313 1.63264 1.64402 1.63227 1.63727 1.63727 |
| | Al ₂ O ₃ Mol % | 0000000 | $\infty \propto \infty \propto \odot \propto \infty \propto \infty \propto \infty \propto \infty$ | | 12222222222222222222222222222222222222 |
| ompositions | BaO Mol % | 40 8 8 4 7 3 3 3 8 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 | 22 22 22 22 22 22 22 22 22 22 22 22 22 | 4 4 5 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 | 22222222222222222222222222222222222222 |
| Ŭ | SiO2 Mol % | \$ 2 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 | 5555556656668 52555566566668 525555566566668 525555556655 52555555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 5255555 52555555 | 2 2 2 2 8 8 9 7 9 4 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 | 82888844444 44 |
| | Melt No. | F1170 F1169 F1168 F1167 F1166 F1165 F1165 | F1119 F1158 F1158 F1158 F1145 F1145 F1145 F1131 F1132 F1133 F1133 F1146 | F1121 F1153 F1143 F1143 F1128 F1129 F1129 F1129 F1134 F1154 | F1161 F1162 F1163 F1163 F1195 F1196 F1196 F1210 F1210 F1200 F1200 F1209 F1209 |

TABLE 7. Ternary BaO-Al₂O₃-SiO₂ compositions

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3.6. The BaO-Al₂O₃-SiO₂ System

Alumina is widely used as a component of glass. Morey [18] states that "alumina in small quantity is a frequent constituent of glass. It gives greater chemical durability, lower coefficient of expansion, and greater freedom from devitrification." It has long been known that small amounts of Al_2O_3 improved the flame working properties of thermometer glass [19].

Aluminate glasses [20, 21] have been of interest because of their improved infrared transmittance as compared to most silicate glasses. An area of glass formation in the CaO-Al₂O₃ system is the basis for these glasses. Aluminosilicate glasses [22] containing 20 to 40 percent Al₂O₃, have high softening temperatures, relatively low thermal expansion coefficients, and high values of hardness. They have been used for lamp envelopes, chemical combustion tubes and "top-of-stove" ware.

The ternary diagram for the $BaO-Al_2O_3-SiO_2$ system [23] has been published along with isofracts for the ternary glasses [24]. More recently Forster et al. [25] have made further studies in this ternary system and have revised the earlier diagram.

The compositions melted in this work are listed in table 7 along with the properties measured on the resulting glasses. The 10 mol percent Al₂O₃ series fall near the phase boundary between the ternary compound BaO \cdot Al₂O₃ \cdot 2SiO₂ and the binary barium silicates. This is illustrated in the ternary diagram shown in figure 39, where the compositions melted and the approximate location of the phase boundaries as determined by Foster et al. [25], and by Thomas [24] are plotted. The refractive index, n_D varied from 1.5940 to 1.6536 with ν in the range from 51.4 to 57.0.

The transmittance curves for 2-mm thicknesses of representative glasses from 6, 8, and 10 mol percent Al₂O₃ series are plotted in figures 40, 41, and 42, respectively. Again, as the Al₂O₃ content of the glasses increase the minimum in transmittance in the 2.75 to 4.0 μ m region moves to higher values. No general explanation of this behavior is readily evident other than that it is related to (OH)⁻ content of the glasses and the manner in which the (OH)⁻ is bound.

The thermal expansion of glass F1123 is shown in figure 43. The linear coefficient of thermal expansion over the temperature range from 100 to 600 °C is 8.1×10^{-6} /°C which is only slightly lower than ordinary window or plate glass. The deformation temperature is 797 °C which is considerably higher than most ordinary glasses.



FIGURE 40. Spectral transmittance of 2-mm thickness of glasses containing 6 mol percent of Al₂O₃.●F1164, × F1166, △ F1169.



FIGURE 41. Spectral transmittance of 2-mm thickness of glasses containing 8 mol percent of Al_2O_3 . \bullet F1124. \times F1132. \triangle F1133.



FIGURE 42. Spectral transmittance of 2-mm thickness of glasses containing 10 mol percent of Al₂O₃. ●F1123, - F1129, ---F1130, × F1143.

4. Analytical Representation of Data

Composition-property data in the six ternary barium silicate glass systems have been quantitatively evaluated following the method of Babcock [3]. Data on refractive index and specific volume, in a number of silicate glass systems, were segregated into groups according to the composition ranges and areas covered by the known primary crystallization phase fields involved. The separate groups of data, one group for each primary phase field, were then subjected to least-squares computer analysis. The program called for determining the role of each oxide in linear equations of the form

$$Glass Property = A SiO_2 + B CaO + C Na_2O + \dots$$

A, B, and C are numerical constants characteristic of the respective oxides and amounts of oxides are expressed in mole fractions. The fidelity with which the equations represent the measured data is indicated by the computerized standard error

$$\sqrt{\frac{\sum (\Delta P)^2}{N-1}}$$



FIGURE 43. Thermal expansion of Glass F 1123 as determined by an interferometric method. Linear coefficient of thermal expansion (100-600 °C) is 8.1 × 10⁻⁶/°C and deformation temperature is 797 °C.

wherein ΔP is the difference between measured and calculated data and N equals the number of measurements.

This work [3] demonstrated that data on several hundred silicate glasses, measured by the National Bureau of Standards and the Geophysical Laboratory, Carnegie Institute of Washington, could be accurately represented to the fourth decimal place by such linear equations. This accuracy was good enough to permit calculation of phase boundaries and compositions of invariant points in binary and ternary silicate glass systems. Approximate phase diagrams were developed in this manner simply by using linear composition-property equations. It follows from this method that boundaries between primary phases are straight lines and that three such property planes may intersect in an invariant point for ternary systems. It must be emphasized that development of an approximate phase diagram in this manner is not meant to replace the wellestablished phase equilibrium methods of Gibbs [26], Morey [27], and others. This quantitative analytical method [3] has two important uses: (1) Formulation of glass compositions for specific property applications, (2) Furnishing first-approximation information on incomplete or nonexistent phase diagrams of silicate glass systems.

A modified procedure has been used for the ternary barium silicates since phase diagrams do not exist for most of these systems. The glasses have been segregated into groups within which the data can be quantitatively represented by linear equations. This procedure made it necessary to adopt an arbitrary criterion for the grouping of glasses. In terms of intended usage of the data and the precision of the measurements, it was decided that the standard error for refractive index for a given group be limited to 0.001. This criterion resulted in placing 71 percent of the glasses in groups which can be referred to here as "compatibility groups." The differences between measured and calculated values, of the other 29 percent, were 0.0020 or greater and were arbitrarily left out of the computerized groups. The interested reader will, of course, draw his own conclusions in this regard and use the measured data and computerized information to fit his own particular needs.

It is pointed out that refractive index, partial dispersions and specific volume are properties of the glasses, but that the ν -value, and its inverse, the dispersive power, are empirical ratios. These properties are linear functions of mole compositions, but the ν -values are not. Linear equations representing ν -values are only first approximations and are shown here for estimation purposes only.

It is also to be noted that the previous work [3] involved a larger number of glasses within groups than were available for the barium silicate glasses. The compositions were chemically analyzed while the barium silicate compositions are calculated from batch compositions. It is to be expected, therefore, that the placement of glasses in given groups and the boundaries between groups will be somewhat less definite in the case of the barium silicate glasses. However, the composition-property information on the barium silicates is quite good enough for the formulation of glasses. As a practical matter the refractive index of a glass depends on the composition, the homogeneity, and the annealing treatment. The determination of the refractive index is dependent upon the precision and accuracy of the measurement process and the environmental conditions of measurement. Unfortunately, annealing procedures cannot be specified quantitatively, and depending on the glass composition in question, may cause differences in the third decimal place in refractive index. To achieve greater precision, say in the fourth or fifth decimal places as in the case of commercial optical glasses, it is necessary to pay much closer attention to all the factors influencing refractive index.

Detailed information on analytical representation of data in the barium silicates is shown in the following sections. Tables 8 to 13 give property-composition equations. Figures 44 to 51 are graphical plots of the derived composition-property relations.

4.1. The BaO-TiO₂-SiO₂ System

Table 8 shows equations relating compositions and properties of glasses in the two compatibility groups in this system. Equations for the partial dispersions are obtained simply by taking differences between the respective refractive index equations. A given partial dispersion may be calculated either by using the partial dispersion oxide factors or by calculating each refractive index and taking differences between the two. The same value will be obtained in the two cases. Calculated values of ν are only first approximations.

TABLE 8. BaO-TiO₂-SiO₂ glasses

| Glass Property = A | $SiO_{i} + B$ | $TiO_2 + C$ | BaO |
|----------------------|---------------|-------------|-----|
|----------------------|---------------|-------------|-----|

| Property | A | В | С | Std. Error |
|---------------------|--------------------------|---------------|-------------|--------------|
| | | Group I Glass | ses | |
| $\overline{n_C}$ | 1.47915 | 2.27530 | 1.84290 | 0.00066 |
| n_D | 1.48163 | 2.29497 | 1.84628 | .00062 |
| n_F | 1.48594 | 2.34396 | 1.85834 | .00070 |
| $n_F - n_D$ | 0.00431 | 0.04899 | 0.01206 | |
| $n_D - n_C$ | .00248 | .01967 | .00338 | |
| $n_F - n_C$ | .00679 | .06866 | .01544 | |
| ν | 60.06 | -43.03 | 41.56 | .4418 |
| Volume | 0.36089 | 0.23177 | 0.08893 | .00078 |
| Average densitie | of differences $= 0.096$ | es between : | measured an | d calculated |
| | | Group II Glas | ses | |
| nc | 1.48429 | 2.32814 | 1.79030 | 0.00116 |
| nn | 1.48553 | 2.35228 | 1.79234 | .00119 |
| n _F | 1.48783 | 2.41798 | 1.79543 | .00127 |
| $n_F - n_D$ | 0.00230 | 0.06570 | 0.00309 | |
| $n_D - n_C$ | .00124 | .02414 | .00204 | |
| $n_F = n_C$ | .00354 | 08984 | .00513 | |

Figure 44 shows compositions of glasses used in the two computerized groups. The position of the boundary between the two groups, shown as a broken line, was obtained by solving the following equations simultaneously

49.93

0.09806

0.1633

.00027

-10.73

0.25306

Average of differences between measured and calculated

41.27

Volume

densities = 0.003

0.34946

I $n_D = 1.48163 \text{ SiO}_2 + 2.29497 \text{ TiO}_2 + 1.84628 \text{ BaO}$ II $n_D = 1.48553 \text{ SiO}_2 + 2.35228 \text{ TiO}_2 + 1.79234 \text{ BaO}$ SiO₂ + TiO₂ + BaO = 1

Solutions and calculation checks are as follows

| SiO ₂ TiO ₂ BaO | 0.35 .30 | SiO ₂ TiO ₂ BaO | 0.55 .20 25 |
|---|-------------|---|-------------------|
| n_D (I) | 1.8533 | Duo | 1.7354 |
| n_D (II) | 1.8529 | | 1.7356 |



FIGURE 44. Compositional plot showing the groups into which glasses in the BaO-TiO₂·SiO₂ system were divided by computer evaluation of property data.

Numbers of glasses in each group are those from earlier composition tables with F omitted.

The averages of differences between measured and calculated densities (reciprocals of the specific volumes) are shown in the tables.

Representation of the data in terms of linear equations permits arranging the information in a number of ways. Figure 45, for example, shows lines of equal n_D in a SiO₂-TiO₂ plot. It will be noted that the equal property lines are continuous across the boundary between the two groups. Similar plots can be made of equal values of partial dispersions and specific volume. Plots showing lines of equal density can be made, but they will



FIGURE 45. Isofracts in the BaO-TiO₂-SiO₂ system.

not be quite linear. Figure 46 shows lines of equal ν in a SiO₂-TiO₂ plot. As previously mentioned, ν is an empirical ratio and the lines of equal value are not continuous across the boundary.

Reference to partial phase diagram information by Rase and Roy [6] and by Cleek and Hamilton [4] suggests that glasses in Group I may lie in the BaO $\cdot 2$ SiO₂ phase field and those in Group II may lie in the BaO \cdot TiO₂ \cdot SiO₂ phase field.



FIGURE 46. Lines of constant ν in the BaO-TiO₂-SiO₂ system.

4.2. The BaO-La₂O₃-SiO₂ System

Table 9 shows equations representing data in the two groups of glasses in this system. It will be noted that La_2O_3 has negative volume factors in both groups. The volume equations represent the density data quite closely.

Figure 47 shows compositions of glasses used in the computerized groups. Information on this system does not permit calculating the exact location of the broken line separating the two groups It is drawn roughly to denote the separation. That glass F549 is in Group I and glass F530 in Group II is verified by the following differences between measured and calculated n_D when equations for the two groups are used

| | Group I | Group II |
|----------------|-----------------|-----------------|
| $F530 \\ F549$ | 0.0023 .0004 | 0.0002 .0039 |

TABLE 9. BaO-La2O3-SiO2 glassesGlass property = A SiO2 + B La2O3 + C BaO

| Property | A | В | С | Std. Error |
|------------------------|--------------------------|--------------|--------------|--------------|
| | (| Group I Glas | ses | |
| nc | 1.48825 | 2.51281 | 1.83983 | 0.00068 |
| n_D | 1.49036 | 2.52380 | 1.84518 | .0006 |
| nr | 1.49538 | 2.55158 | 1.85810 | .00070 |
| $n_F - n_D$ | 0.00502 | 0.02778 | 0.01292 | |
| $n_D - n_C$ | .00211 | .01099 | .00535 | |
| $n_F - n_C$ | .00713 | .03877 | .01827 | |
| ν | 63.00 | 6.90 | 41.88 | 0.0913 |
| Volume | 0.35428 | -0.17875 | 0.10807 | .00076 |
| Average o densities | of differences $= 0.009$ | s between | measured and | d calculated |

| | | 0 | noup ii oius | 505 | |
|-------------|------|-------------|--------------|--------------|------------|
| n_c | | 1.51660 | 2.46619 | 1.79980 | 0.00037 |
| n_D | | 1.51872 | 2.47735 | 1.80510 | .00039 |
| n_F | | 1.52372 | 2.50559 | 1.81819 | .00039 |
| $n_F - n_D$ | | 0.00500 | 0.02824 | 0.01309 | |
| $n_D - n_C$ | | .00212 | .01116 | .00530 | |
| $n_F - n_C$ | | .00712 | .03940 | .01839 | |
| ν | | 63.54 | 5.35 | 40.78 | 0.0965 |
| Volume | | 0.32645 | -0.10865 | 0.14791 | .00030 |
| Average | of | differences | between a | measured and | calculated |
| densiti | es = | 0.005 | | | |



FIGURE 47. Compositional plot showing the groups into which glasses in the BaO-La₂O₃-SiO₂ system were divided by computer evaluation of property data.

Numbers of glasses in each group are those from earlier composition tables with F omitted.

4.3. The BaO-Ta₂O₅-SiO₂ System

Table 10 shows equations representing data in the three groups in this system. It will be noted that Ta_2O_5 has negative ν in all groups and negative volume factors in groups I and II.

Figure 48 shows compositions of glasses used in the computerized groups. The data are not sufficient to allow calculation of the boundaries between the three groups. The broken lines roughly indicate the separations. Calculation of n_p for the four glasses near boundaries, F588, F534, F592, and F542 indicates that the glasses have been correctly grouped. The following indicates differences between measured and calculated n_p using the indicated equations:

TABLE 10. BaO-Ta₂O₅-SiO₂ glasses

Glass property = $A \operatorname{SiO}_2 + B \operatorname{Ta}_2 \operatorname{O}_5 + C \operatorname{BaO}$

| Glass Property | A | В | | | С | I | Std. Error |
|---------------------|-------------|----------|--------|-------|--------|-------|------------------|
| | 1 | Group I | Glas | ses | | | |
| ne | 1.43819 | 2.68 | 3156 | 1.9 | 5482 | 0. | 00028 |
| nD | 1.43974 | 2.70 | 166 | 1.9 | 6134 | | 00028 |
| n_F | 1.44331 | 2.75 | 161 | 1.9 | 7761 | | 00028 |
| $n_F - n_D$ | 0.00357 | 0.04 | 995 | 0.0 | 1627 | | |
| $n_D - n_C$ | .00155 | .02 | 010 | .0 | 0652 | | |
| $n_F - n_C$ | .00512 | .07 | '005 | .0 | 2279 | | |
| ν | 65.77 | -96.27 | , | 34.1 | 3 | 0. | 2208 |
| Volume | 0.37394 | -0.34 | 930 | 0.0 | 6008 | | 00077 |
| Average | of differen | ces betw | een | measu | red ar | nd c | alculated |
| densitie | s = 0.007 | | _ | | | | |
| | | Group I | [Glas | sses | | | |
| ne | 1 50395 | 2.48 | 739 | 1.8 | \$5520 | 0 | 00048 |
| ne | 1.50627 | 2.50 | 586 | 1.8 | 6048 | | 00048 |
| n_{ν} | 1.51030 | 2.50 | 296 | 1.0 | 7262 | • | 00045 |
| $n_{\nu} - n_{\nu}$ | 0.00463 | 0.06 | 710 | | 1214 | | 00010 |
| $n_P - n_C$ | 00172 | 01 | 847 | 0.0 | 0528 | | |
| $n_{\nu} - n_{C}$ | 00635 | 08 | 557 | 0.0 | 1742 | 1 | |
| ν | 59.09 | - 85.41 | | 47.2 | 8 | 0 | 4249 |
| Volume | 0.31595 | -0.16 | 059 | 01 | 4165 | . | 00071 |
| Average | of differen | ces betw | een | measu | red ar | nd e | alculated |
| densitie | s = 0.010 | | | | | | and different of |
| | | Group Il | I Gla | sses | | | |
| nc | 1 65915 | 2 31 | 775 | 16 | 9455 | 0 | 00003 |
| no | 1.66596 | 2.33 | 911 | 1.6 | 9456 | | 00000 |
| nr | 1.67132 | 2.36 | 772 | 1.7 | 0992 | | 00004 |
| $n_F - n_D$ | 0.00536 | 0.02 | 861 | 0.0 | 1536 | | |
| $n_D - n_C$ | .00681 | .02 | 136 | .0 | 0001 | | |
| $n_F - n_C$ | .01217 | .04 | 997 | .0 | 1537 | | |
| ν | 50.87 | - 12.64 | | 46.8 | 7 | 0. | 2008 |
| Volume | 0.24761 | 0.02 | 726 | 0.1 | 9721 | | 00009 |
| Average | of differen | ces betw | een | measu | red ar | id ca | alculated |
| densitie | s = 0.002 | | | | | | |
| = | | | | | | | |
| | | Group I | Gro | up II | Group | III | |
| | F588 | 0.0001 | 0 | 0026 | | | |

F534

F592

F542

.0026

.0006

.0001

.0028

0.0014

.0000



FIGURE 48. Compositional plot showing the groups into which glasses in the BaO-Ta₂O₅-SiO₂ system were divided by computer evaluation of property data.

Numbers of glasses in each group are those from earlier composition tables with F omitted.

4.4. The BaO-ZnO-SiO₂ System

Table 11 shows composition-property equations for glasses in the five groups in this system. This table identified glasses placed in the different groups. Figure 49 gives compositions of the 57 glasses used in the evaluations. The broken lines serve to separate the five groups. Exact composition locations of the boundaries could not be calculated. The equations indicate that the property contributions of ZnO and BaO, in terms of their factors, are similar quantitatively. In this connection, all 57 glasses were run as one group on the computer. The resulting n_D equation in this case was $n_D = 1.47000$ $SiO_2 + 1.81955$ ZnO + 1.87614 BaO with a standard error of 0.00205. Differences between measured and calculated n_D ranged from -0.0073 to 0.0038. However, the range of standard errors for n_D for the five separate groups from 0.00048 to 0.00064 indicates proper placement of the glasses. The interested reader can determine by calculation that n_D values, for example, of glasses not used in groups, have measured minus calculated differences greater than 0.001.

| | IABLE I | II. DaU-ZnU- | SIO ₂ grasses | |
|----------------|----------------------|---------------------------------------|--------------------------|---------------|
| | Glass pro | $operty = A \operatorname{SiO}_2 + A$ | B ZnO + C BaO | |
| Glass | A | В | С | Std. |
| property | | | | Error |
| Group I | Glasses: a 70 | 5, 698, 706, 7 728, 695 | 707, 727, 693, | 694, 702, 709 |
| | 703, 710, 730, | 712, 718, 731 | , 784, 714, 766 | 5, 713 |
| ne | 1.46539 | 1.80155 | 1.88253 | 0.00065 |
| np | 1.46731 | 1.80723 | 1.88812 | .00064 |
| n _F | 1.47172 | 1.82073 | 1.90237 | .00064 |
| $n_F - n_D$ | 0.00441 | 0.01350 | 0.01425 | |
| $n_D - n_C$ | .00192 | .00508 | .00339 | |
| ν | 64.55 | 33.86 | 39.39 | 0.1057 |
| Group II | [Glasses: 809 80 | 9, 813, 803, 8 14, 839, 807, 7 | 02, 801, 797, 99, 755 | 798, 806, 842 |
| ne | 1.46248 | 1.81986 | 1.88284 | 0.00056 |
| no | 1.46422 | 1.82590 | 1.88864 | .00057 |
| nr | 1.46800 | 1.84130 | 1.90279 | .00058 |
| $n_F - n_D$ | 0.00378 | 0.01540 | 0.01415 | |
| $n_D - n_C$ | .00174 | .00604 | .00580 | |
| $n_F - n_C$ | .00552 | .02144 | .01995 | |
| ν | 63.73 | 32.00 | 42.13 | 0.1076 |
| Gi | oup III Glasse | es: 733, 734, 7 | 794, 735, 841, | 795, 840 |
| n _C | 1.52488 | 1.74916 | 1.74302 | 0.00047 |
| n_D | 1.52747 | 1.75428 | 1.74696 | .00048 |
| n_F | 1.53373 | 1.76683 | 1.75636 | .00050 |
| $n_F - n_D$ | .00626 | .01255 | 0.00940 | |
| $n_D - n_C$ | .00259 | .00512 | .00394 | |
| $n_F - n_C$ | .00885 | .01767 | .01334 | |
| ν | 58.21 | 37.56 | 55.81 | 0.0833 |
| Group 1 | IV Glasses: 74 | 5, 721, 724, 7 | 54, 723, 722, | 775, 720, 715 |
| nc | 1.49409 | 1.84200 | 1.80081 | 0.00051 |
| n _D | 1.49602 | 1.84844 | 1.80587 | .00051 |
| n_F | 1.50064 | 1.86444 | 1.81811 | .00053 |
| $n_F - n_D$ | 0.00462 | 0.01600 | 0.01224 | |
| $n_D - n_C$ | .00193 | .00644 | .00506 | |
| $n_F - n_C$ | .00655 | .02244 | .01730 | |
| ν | 63.29 | 28.97 | 45.02 | 0.0827 |
| | Group V Glas | ses: 760, 786 | , 787, 764, 762 | 2, 788 |
| nc | 1.46984 | 1,75656 | 1.89008 | 0.00056 |
| nD | 1.47139 | 1.76190 | 1.89640 | .00056 |
| n _F | 1.47458 | 1.77476 | 1.91280 | .00056 |
| $n_F - n_D$ | 0.00319 | 0.01286 | 0.01640 | |
| $n_D - n_C$ | .00155 | .00534 | .00632 | |
| $n_F - n_C$ | .00474 | .01820 | .02272 | 1 N |
| ν | 69.07 | 38.17 | 30.43 | 0.0652 |
| | | | | |

D 0 7 0

^aNumbers of Glasses in each group are those from earlier composition tables with F omitted.

4.5. The BaO-Nb₂O₅-SiO₂ System

Table 12 gives equations for glasses in the two groups in this system. It will be noted that ν values for Nb₂O₅ are negative.



FIGURE 49. Compositional plot showing the groups into which glasses in the BaO-ZnO-SiO₂ system were divided by computer evaluation of property data.

Figure 50 shows compositions of glasses used in the two computer groups. The position of the boundary between the groups, indicated by a broken line, was determined by solving the following equations simultaneously

I $n_D = 1.49408 \operatorname{SiO}_2 + 2.80691 \operatorname{Nb}_2O_5 + 1.85111 \operatorname{BaO}$ II $n_D = 1.56558 \operatorname{SiO}_2 + 2.69145 \operatorname{Nb}_2O_5 + 1.78584 \operatorname{BaO}$ SiO₂ + Nb₂O₅ + BaO = 1

Solutions and calculation checks are as follows

| SiO ₂ Nh ₂ O ₅ | 0.477 | 0.516 |
|--|--------|--------|
| BaO | .523 | .384 |
| $n_{D}(\mathbf{I})$ | 1.6808 | 1.7624 |
| $n_D(\mathrm{II})$ | 1.6808 | 1.7627 |

TABLE 12. BaO-Nb₂O₅-SiO₂ glasses

Glass property = $A \operatorname{SiO}_2 + B \operatorname{Nb}_2 O_5 + C \operatorname{BaO}$

| Glass property | A | В | С | Std. Error |
|---|---|--|---|---------------------------------------|
| | | Group I Glasse | s | |
| n_{C} n_{D} n_{F} $n_{F} - n_{D}$ $n_{D} - n_{C}$ $n_{F} - n_{C}$ ν | $\begin{array}{c} 1.49209\\ 1.49408\\ 1.49870\\ 0.00462\\ .00199\\ .00661\\ 59.38\end{array}$ | 2.78035 2.80691 2.87595 0.06904 .02656 .09560 -103.22 | $\begin{array}{c} 1.84569\\ 1.85111\\ 1.86462\\ 0.01351\\ .00542\\ .01893\\ 43.03\end{array}$ | 0.00053 .00053 .00055 0.3705 |
| | | Group II Glasse | s | |
| n_C n_D n_F $n_F - n_D$ $n_D - n_C$ $n_F - n_C$ ν | 1.56263 1.56558 1.57170 0.00612 .00295 .00907 42.36 | $\begin{array}{r} 2.66145\\ 2.69145\\ 2.77114\\ 0.07969\\ .03000\\ .10969\\ -35.25\end{array}$ | $\begin{array}{c} 1.78253\\ 1.78584\\ 1.79431\\ 0.00847\\ .00331\\ .01178\\ 47.86\end{array}$ | 0.00112 .00110 .00109 0.3004 |



FIGURE 50. Compositional plot showing the groups into which glasses in the $Ba-Nb_2O_5-SiO_2$ system were divided by computer evaluation of property data.

Numbers of glasses in each group are those from earlier composition tables with F omitted.

4.6. The BaO-Al₂O₃-SiO₂ System

Table 13 gives composition-property equations for the two groups of glasses in this system. Phase diagrams for this ternary system and the three binary systems have been published [23, 24, 25]. Figure 51 is a mol fraction plot converted from published diagrams 210 and 556 [23]. This figure shows the compositions of glasses used in computerized groups. Glasses situated in the solid solution area of BaO · 2SiO₂ and 2BaO · 3SiO₂ were placed in Group I. Those in the BaO \cdot Al₂O₃ \cdot 2SiO₂ primary phase field were placed in Group II. In each case the criterion, previously mentioned, for "compatibility groups" was adhered to. Location of the boundary between the two groups cannot be calculated exactly as was the case in some of the other systems.

TABLE 13. BaO-Al2O3-SiO2 glasses

Glass Property = $A \operatorname{SiO}_2 + B \operatorname{Al}_2 \operatorname{O}_3 + C \operatorname{BaO}$

| Property | A | В | С | Std. Error | | |
|---|------------------------------|---------------|-------------------|-----------------|--|--|
| Group I Glasses: a 1131, 1132, 1133, 1164, 1165, 1166 | | | | | | |
| Solid Sol | ution of BaO \cdot 2 | 2SiO2 and 2Ba | $aO \cdot 3SiO_2$ | | | |
| n_c | 1.56751 | 1.38164 | 1.75764 | 0.00029 | | |
| n_D | 1.57129 | 1.37834 | 1.76167 | .00032 | | |
| n_F | 1.57893 | 1.38051 | 1.77168 | .00032 | | |
| $n_F - n_D$ | 0.00764 | 0.00217 | 0.01001 | | | |
| $n_D - n_C$ | .00378 | -0.00330 | .00403 | | | |
| $n_F - n_C$ | .01142 | -0.00113 | .01404 | | | |
| ν | 50.05 | 95.47 | 53.80 | 0.2210 | | |
| Group II | Glasses: 1143. | 1123, 1128, 1 | 129, 1130, 119 | 06. 1197. 1198. | | |
| | 1210, 1207, 1211, 1209, 1208 | | | | | |
| BaO · Al ₂ | 2O3 · 2SiO2 Prim | ary Phase | | | | |
| n_C | 1.48964 | 1.57531 | 1.82391 | 0.00074 | | |
| n_D | 1.49166 | 1.57848 | 1.82924 | .00075 | | |
| n_F | 1.49601 | 1.58578 | 1.84299 | .00076 | | |
| $n_F - n_D$ | 0.00435 | 0.00730 | 0.01375 | | | |
| $n_D - n_C$ | .00202 | .00317 | .00533 | | | |
| $n_F - n_C$ | .00637 | .01047 | .01908 | | | |

^a Numbers of Glasses in each group are those from earlier composition tables with F omitted.

36.61

55.62

0.2063

66.90

ν

Previous work [3] has indicated that oxide factors for refractive index are characteristic of the primary phase field involved. For example, the n_D factors for SiO₂ in SiO₂ fields (particularly cristobalite and tridymite) is reasonably close to 1.458, the refractive index n_D for fused silica. Likewise the specific volume factor for such glasses corresponds to a density of 2.20 approximating the density of fused silica. The n_D factor of 1.57848 for glasses in Group II is reasonably close to those found for Al₂O₃ in other glass systems [3]. However, the 1.37834 n_D factor for Al₂O₃ for glasses in Group I is low and suggests the need for more data in this area.



FIGURE 51. Triangular plot showing the phase fields and groups into which glasses in the BaO-Al₂O₃-SiO₂ system were divided by computer evaluation of property data.

5. Formulation of Glasses for Specific Optical Applications

The glass technologist and optical designer can use the foregoing quantitative relations between glass compositions and properties to calculate compositions having desired optical properties. The use of this method [3] must be based on reliable experimental data. The data shown in this report are considered to meet this criterion. The method can best be understood by outlining examples of its use.

5.1. Example One

Values of n_p in Group I TiO₂ glasses can be determined using the equation: $n_p = 1.48163$ SiO₂+2.29497 TiO₂+1.84628 BaO. Consider glass F35 having a calculated $n_p = 1.67236$. It is desired to increase the index by 0.0050. This can be done in three ways: (1) substitution of TiO₂ for SiO₂, (2) substitution of BaO for SiO₂. or (3) substitution of TiO₂ for BaO. Differences between factors for these substitutions are respectively 0.81334, 0.36465, and 0.44869. The composition change for the first substitution is 0.0050/0.81334=0.0061 TiO₂ for SiO₂. The others are determined in the same manner. The following table shows compositions and calculated values for n_D , mean dispersion $n_F - n_C$, ν , and densities for the four glasses.

| | F35 | (1) | (2) | (3) |
|---|---------|---------|---------|---------|
| SiO_{2} TiO_{2} BaO n_{D} $n_{F} - n_{C}$ ν Density | 0.6000 | 0.5939 | 0.5863 | 0.6000 |
| | .1000 | .1061 | .1000 | .1111 |
| | .3000 | .3000 | .3137 | .2889 |
| | 1.67236 | 1.67732 | 1.67736 | 1.67734 |
| | 0.01558 | 0.01594 | 0.01569 | 0.01616 |
| | 44.20 | 43.57 | 43.95 | 43.27 |
| | 3.754 | 3.765 | 3.807 | 3.732 |

5.2. Example Two

Consider glass F1432 in Group I Nb₂O₅ glasses which has a measured n_D of 1.63471. It is desired to calculate the exact composition having this index value. Since it contains three oxides one must be fixed arbitrarily. Assume that SiO₂=0.66. The solution is obtained by solving these equations simultaneously:

 $n_D = 1.49408 \text{ SiO}_2 + 2.80691 \text{ Nb}_2\text{O}_5 + 1.85111 \text{ BaO}$ SiO₂ + Nb₂O₅ + BaO = 1

Then; 1.63471 = 1.49408 (.66) + 2.80691 Nb₂O₅ + 1.85111 (0.34 - Nb₂O₅)

| | Glass F1432 | Calculated |
|-----------------------|----------------|-------------|
| SiO_2 | 0.6600 | 0.6600 |
| Nb_2O_5 | .0200 | .0201 |
| BaO | .3200 | .3199 |
| n_D | 1.63471 | 1.63468 |
| $n_F - n_C$ | 0.01241 | 0.01234 |
| ν | 51.10 | 50.87 |
| (Measured table 6) | values for F14 | 32 are from |

5.3. Example Three

Glass F583 in Group II Ta₂O₅ glasses has a measured mean dispersion of 0.01612. Calculate the exact composition assuming SiO₂=0.53. The answer is obtained from the equation:

0.01612 = 0.00635 (0.53) + 0.08557 (0.47 - BaO) + 0.01742 BaO

| | F583 (Table 4) | Calculated | |
|---|--|--|--|
| SiO_{2} $Ta_{2}O_{5}$ BaO n_{D} $n_{F} - n_{C}$ ν Density | $\begin{array}{c} 0.5300\\ .0700\\ .4000\\ 1.71844\\ 0.01612\\ 44.60\\ 4.703\end{array}$ | $\begin{array}{r} 0.5300\\ .0670\\ .4030\\ 1.71598\\ 0.01612\\ 44.65\\ 4.678\end{array}$ | |
| | | | |

5.4. Example Four

Glass F553 in Group II La_2O_3 glasses has a measured density of 4.387 (volume = 0.22795). Assume SiO₂=0.55 and calculate exact composition. The solution is given by: 0.22795 = 0.32645 (0.55) = 0.10865 $La_2O_3 + 0.14791$ (0.45 - La_2O_3)

| | F553 (Table 3) | Calculated |
|----------------------|----------------------|--------------------|
| SiO2 La2O2 | 0.5500 | 0.5500 |
| BaO Density | $.3800 \\ 4.387$ | .3792 4.387 |
| n_D $n_F - n_C$ | $1.69496 \\ 0.01369$ | 1.69519 0.01368 |
| ν | 50.80 | 50.79 |

5.5. Example Five

Figure 45 shows lines of equal n_D in the TiO₂ glasses and figure 46 shows lines of constant ν in this system. Superposition of these two figures indicates that the 1.75 n_D line crosses the 35 ν line in Group I. However, the 1.75 n_D line crosses the 30 ν line in Group II glasses. Calculate the two compositions.

(a) Composition of the glass having an n_D of 1.75 and a ν of 35 is obtained by solving the following equations simultaneously:

$$1.75 = 1.48163 \text{ SiO}_2 + 2.29497 (1 - \text{SiO}_2 - \text{BaO}) + 1.84628 \text{ BaO}$$

35 = 60.06 SiO₂ - 43.03 (1 - SiO₂ - BaO) + 41.56 BaO

The composition is found to be:

| SiO_2 | 0.4918 | | |
|---------|--------|--|--|
| TiO_2 | .1851 | | |
| BaO | .3231 | | |

A check calculation shows the values as 1.75000 and 35.01.

(b) Composition of the glass having an n_D of 1.75 and a ν of 30 is obtained by solving the equations:

$$1.75 = 1.48553 \text{ SiO}_2 + 2.35228 (1 - \text{SiO}_2 - \text{BaO}) + 1.79234 \text{ BaO}$$

$$30 = 41.27 \operatorname{SiO}_2 - 10.73 (1 - \operatorname{SiO}_2 - \operatorname{BaO}) + 49.93 \operatorname{BaO}$$

The composition is:

| SiO_2 | 0.5852 |
|---------|--------|
| TiO_2 | .2450 |
| BaO | .1698 |

A check calculation gives the values as 1.74998 and 30.00.

6. Summary

The areas of glass formation in the following ternary oxide systems have been determined: BaO-TiO₂-SiO₂ BaO-La₂O₃-SiO₂ BaO-Ta₂O₅-SiO₂ BaO-ZnO-SiO₂ BaO-Nb₂O₅-SiO₂ BaO-Al₂O₃-SiO₂

Property measurements, including sag point, refractive index and dispersion, liquidus temperature, and infrared transmittance, were made on the resulting glasses. In addition, composition-property data were evaluated to develop quantitative relations for use by glass technologists in formulating glasses having specific property values.

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