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Properties of Barium Titanium Silicate Glasses [1,2]

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The glass-forming region of the BaO-TiO_2-SiO_2 system has been determined. The refractive index, n_D, nu value, liquidus temperature, and transmittances in the near infrared have been measured. Also measured for representative glasses were linear coefficient of thermal expansion, deformation temperature, chemical durability, and hygroscopicity. A number of stable glasses were found, which have high refractive indices, good infrared transmittances, and high deformation temperatures, and which are unique in their resistance to attack by both acids and alkalis.

1. Introduction

The development of infrared detecting devices has created a demand for glasses for their construction. Many of these devices operate in the near infrared at the wavelengths of the so-called atmospheric windows, where atmospheric transmittance is high. The windows for which glasses are being developed are those at wavelengths of roughly 2.0 to 2.4 and 3.5 to 6.0 μ.

The requirements for the glasses include high transmittance at the wavelengths of interest, and good chemical durability. In addition, for refracting optics, glasses having high refractive indices over the range of about 1.80 to 2.00, and a range of dispersions for each index, are needed. B_2O_3 and P_2O_5 are not desirable as constituents of infrared transmitting glasses, as they cause rather strong absorption bands beyond wavelengths of about 2.75 μ [1].[3] The silicate glasses, in general, do not transmit beyond about 5 μ, presumably due to the Si-O bond, which absorbs at 4.45 μ [2]. Germanate glasses transmit to about 6 μ [1], but GeO_2 is a scarce and expensive material so that it is not readily available as a constituent of glass. Another group of oxide glasses, which contain no so-called "glass former," are the calcium aluminate glasses [1], which also transmit to about 6 μ. They require very high melting temperatures, devitrify easily, and have poor chemical durability.

Most high-index glasses presently available are either extra-dense flint glasses, which have a high PbO content, or rare-earth borate glasses [3]. The extra-dense flint glasses have fairly good infrared transmittances, cutting off, as do most silicate glasses, at about 5 μ. They have high refractive indices, but their chemical durability is poor. The B_2O_3 content of most rare-earth glasses makes them useless for infrared applications.

Upon consideration of the above factors, it was decided that silicate glasses appear to offer the best possibilities for general use if other components could be found to impart the desired properties to the glasses. A system on which little information was available, but which appeared promising from the point of view of high refractive index and good infrared transmittance if glass-forming compositions could be found, was the ternary BaO-TiO_2-SiO_2 system. The phase equilibrium diagram has not been determined, but information is available on the binary sides of the ternary system [4, 5, 6]. Rase and Roy have determined the liquidus temperatures and phase relations along the line $BaO{\cdot}TiO_2$-SiO_2 in the ternary diagram [7]. This information was very useful in selecting compositions in the ternary system that could be melted and cooled as glasses.

2. Experimental Procedure

The glasses were 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, 2½ in. in diameter by 3 in. deep. After the batch was melted, the melt was stirred for 2 hr with a motor-driven platinum–10-percent-rhodium double-bladed propeller-type stirrer. It was then poured into a heated metal mold to form a block about ½ in. thick. When sufficiently rigid, the glass block was transferred to an electric muffle furnace, which was cooled to room temperature in approximately 18 hr. Only those compositions that could be melted below 1,500° C and in which no appreciable devitrification occurred during cooling were considered to produce glasses. These experimental conditions were used to define the glass-forming region of the system, and no attempt was made to enlarge the region by melting at higher temperatures or by cooling the melts more rapidly to avoid devitrification.

A softening temperature for each glass was determined by a gradient method [8]. A fiber of glass, 0.4 to 0.6 mm in diameter, was supported at approximately ½-in. intervals on a platinum holder and placed in a known temperature gradient for 20 to 30 min. From the position at which the fiber sagged between supports, the softening temperature could be determined to ± 10 deg C. The softening temperature, so determined for these glasses, was found to be from 40 to 60 deg C above the deformation point as determined by the interferometric thermal-expansion method [9]. Using this information, the glasses were annealed by heating for 4 to 6 hr at a temperature about 60 deg C below their softening temperature and then cooling at a rate of 2½ deg/hr to 350° C. It is believed that this treatment yielded glasses of comparable annealing, inasmuch as the temperature at which equilibrium was obtained would be a function of the composition and rate of cooling.

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[2] Presented at the Fifty-Seventh Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 27, 1955 (Glass Division No. 32).

[3] Figures in brackets indicate the literature references at the end of this paper

The liquidus temperature of each glass was determined by a temperature-gradient method [10].

Refractive-index determinations were made on polished annealed samples of the glasses in the form of 60° prisms for the C, D, and F lines by the NBS Optical Instruments Section. The spectral transmittances of the glasses were determined from 1.0 to 6.0 μ by the NBS Radiometry Section, with a model 21 double-beam Perkin-Elmer infrared spectrometer.

The chemical durability of the glasses was determined by an interferometric method developed by Hubbard and Hamilton [11]. Cloth-polished samples were immersed about one-half their lengths in solutions buffered to the desired values of pH. After 6 hr of exposure at 80° C the samples were removed from the solutions and viewed through an optical flat with monochromatic light. Any shift in the interference bands as they pass from the unexposed to the exposed portion of a sample is proportional to the amount of attack by the buffered solution and is, therefore, a measure of the chemical durability of the glass.

The linear thermal expansions and the deformation temperatures of several of the glasses were determined by an interferometric method described by Saunders [9].

3. Results

3.1. Glass-Forming Area of the BaO-TiO_2-SiO_2 System

The compositions of all melts made in the system are given in table 1 and are plotted in the ternary

TABLE 1. *Ternary* BaO–TiO_2–SiO_2 *Compositions*

Melt	Composition			n_D	ν	Liquidus temperature	Remarks
	SiO_2	BaO	TiO_2				
	Mole %	*Mole %*	*Mole %*			*° C*	
F294	65	20	15	--------	----	1,468	Devitrified in mold.
F293	60	20	20	--------	----	1,484	Do.
F292	55	20	25	--------	----	1,462	Do.
F291	50	20	30	--------	----	1,464	Do.
F300	45	20	35	--------	----	1,488	Do.
F316	40	20	40	--------	----	>1,447	Do.
F331	35	20	45	--------	----	>1,440	Do.
F332	30	20	50	--------	----	>1,440	Do.
F337	25	20	55	--------	----	>1,440	Do.
F363	55	22.5	22.5	--------	----	>1,400	Do.
F364	42.5	22.5	35	--------	----	1,248	Some devitrification.
F365	32.5	22.5	45	--------	----	1,339	Considerable devitrification.
F151	70	25	5	--------	----	1,408	Do.
F150	65	25	10	--------	----	1,345	Do.
F149	60	25	15	--------	----	1,265	Opal in center.
F148	55	25	20	1.73021	34.0	1,250	Glass.
F147	50	25	25	1.77760	30.6	1,248	Do.
F146	45	25	30	1.82236	27.6	1,233	Do.
F145	40	25	35	1.86682	25.3	1,218	Do.
F289	35	25	40	--------	----	1,242	Dark-brown glass.
F317	30	25	45	--------	----	1,260	Do.
F333	25	25	50	--------	----	1,305	Black glass.
F367	22.5	25	52.5	--------	----	1,310	Considerable devitrification.
F336	20	25	55	--------	----	1,333	Contained devitrification.
F366	27.5	27.5	45	--------	----	1,266	Considerable devitrification.
F368	37.5	27.5	35	--------	----	1,288	Do.
F152	65	30	5	1.63139	49.9	1,356	Glass.
F35	60	30	10	1.67250	43.7	1,301	Do.
F49	55	30	15	1.71275	38.6	1,330	Do.
F40	50	30	20	1.75412	34.3	1,342	Do.
F95	45	30	25	1.79585	30.9	1,344	Do.
F138	40	30	30	1.83697	28.1	1,350	Do.
F139	35	30	35	1.87998	25.8	1,337	Some devitrification in end of block.
F288	35	30	35	--------	----	1,354	Some devitrification in block.
F290	30	30	40	--------	----	1,313	Considerable devitrification.
F334	25	30	45	--------	----	1,331	Do.
F335	20	30	50	--------	----	1,302	Do.
F353	33.3	33.3	33.3	--------	----	1,405	Devitrified in mold.
F144	60	35	5	1.65158	49.0	1,367	Glass.
F143	55	35	10	1.69148	43.1	1,354	Do.
F142	50	35	15	1.73037	38.3	1,393	Do.
F141	45	35	20	--------	----	1,415	Considerable devitrification.
F140	40	35	25	--------	----	1,420	Do.
F315	35	35	30	--------	----	1,423	Devitrified in mold.
F287	30	35	35	--------	----	1,441	Do.
F282	55	40	5	--------	----	1,375	Cloudy.
F283	50	40	10	--------	----	1,401	Some devitrification spots.
F284	45	40	15	--------	----	1,441	Considerable devitrification.
F295	40	40	20	--------	----	1,462	Devitrified in mold.
F285	35	40	25	--------	----	1,468	Do.
F286	30	40	30	--------	----	1,484	Do.
F296	50	45	5	--------	----	1,404	Do.
F297	45	45	10	--------	----	1,462	Do.
F298	40	45	15	--------	----	1,462	Do.
F299	35	45	20	--------	----	1,488	Do.

diagram in figure 1. As may be seen from the figure, the longest BaO isopleth along which glasses are formed is the 25 mole percent BaO line. Although glasses are not formed on this line to the BaO-SiO_2 binary, glass formation begins at about 20 mole percent of TiO_2 and extends to relatively high concentrations of TiO_2. 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 TiO_2 content was increased. Those containing up to about 15 mole percent of TiO_2 were nearly colorless, whereas those containing intermediate amounts, from 20 to 35 mole percent of TiO_2, were orange colored, and the others having above 40 mole percent of TiO_2 were dark brown to black. Evidently, as the TiO_2 content is increased, the absorption increases at the shorter wavelengths in the visible region, and at higher TiO_2 concentrations very little visible light is transmitted.

3.2. Liquidus Temperature

The liquidus temperature 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 than 1,400° C. The lowest liquidus temperatures were found along the 25-mole-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-mole-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 [12]. Probably, the ease of glass formation is related to the degree of dissociation of the primary phase in the melt, because a similar observation was made for the BaO–B_2O_3–SiO_2 glasses [8]. In the latter 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.

3.3. Refractive Indices and Dispersions

The refractive indices, n_D, and ν values are plotted in figure 2 for the three BaO isopleths along which glasses were obtained. The values of n_D varied from 1.63139 to 1.87998, and ν from 49.9 to 25.3. The refractive-index values appear to be linear functions of composition. The plots of the ν values definitely show curvature.

3.4. Infrared Transmittances

Figures 3 to 9, inclusive, give the transmittances for 2-mm thicknesses of the ternary glasses over the spectral range 1 to 5 μ. The figures compare glasses of constant TiO_2 content. In general, the glasses giving the highest transmittance at 4 μ lie on the 30-mole-percent BaO isopleth up to a TiO_2 concentration of 25 mole percent, then the compositions shift to the 25-mole-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.

3.5. Chemical Durability and Hygroscopicity

The values of chemical durability of five representative ternary glasses are given in table 2 and are plotted as a function of pH in figure 10. All values are for 6 hr of exposure at 80° C. As may be seen from the figure, the glass containing 60 mole percent of SiO_2 is attacked in the alkaline range. As SiO_2 is replaced by TiO_2, the attack in this range is decreased, and although slight attack or swelling is noticed at pH 2, the glasses containing 20 mole percent, and more, of TiO_2 show no attack in the alkaline range.

The hygroscopicity [13], 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.

TABLE 2. *Hygroscopicity and chemical durability of* BaO–TiO_2–SiO_2 *glasses*

Melt	Water sorbed		Surface alteration, [a] fringes, at pH— (exposures, 6 hr at 80° C)					
	1 hr	2 hr	2.0	4.1	6.0	8.2	10.2	11.8
	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 3/4 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.

3.6. Thermal Expansion and Deformation Temperatures

The linear coefficient of thermal expansion has been determined for only three representative ternary glasses. The values obtained were 9 or 10×10^{-6}, 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 the three glasses are plotted in figure 12. The deformation temperatures varied from 767° C for glass F35, containing 10 mole percent of TiO_2, to 791° C for glass F138, having 30 mole percent of TiO_2.

4. Summary

The glass-forming region of the $BaO-TiO_2-SiO_2$ system has been determined. The liquidus temperature, refractive indices and dispersions, and infrared transmittances of the glasses have been measured. The chemical durability and hygroscopicity, and linear thermal expansion of selected glasses have been determined. Glasses in this system are unique as compared to most glasses in that they have a high deformation temperature, exceptional chemical durability, and very low hygroscopicity.

5. References

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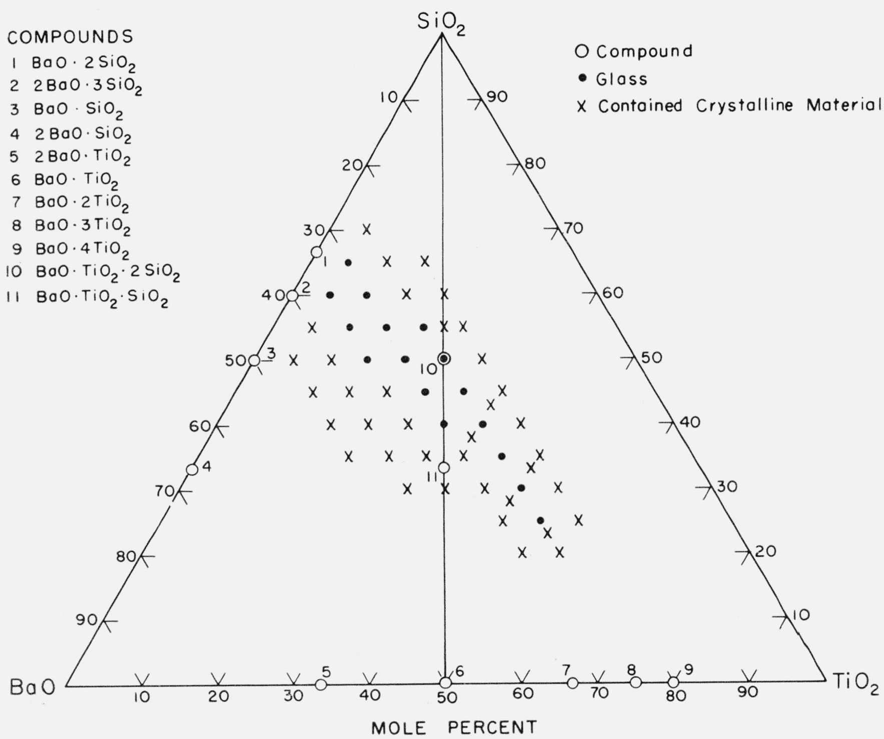

FIGURE 1. *Compositions (in mole percent) studied in the system* $BaO-TiO_2-SiO_2$.

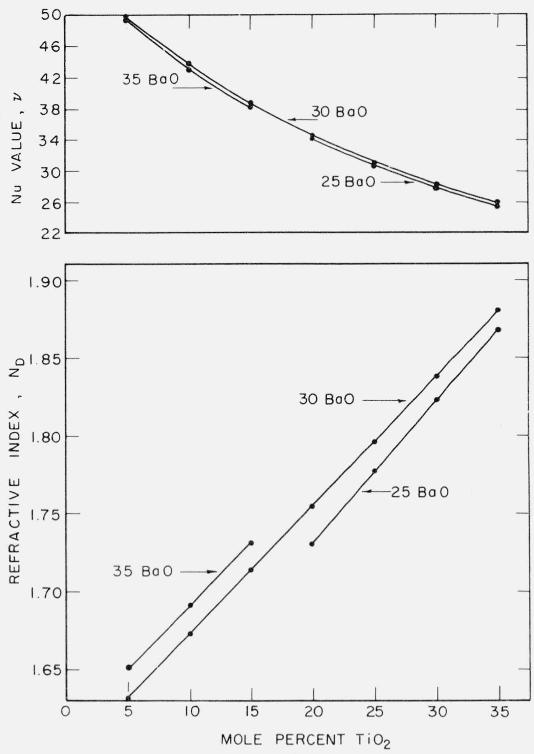

FIGURE 2. *Plot of refractive index and nu value as a function of composition for the glass-forming compositions in the* $BaO–TiO_2–SiO_2$ *system.*

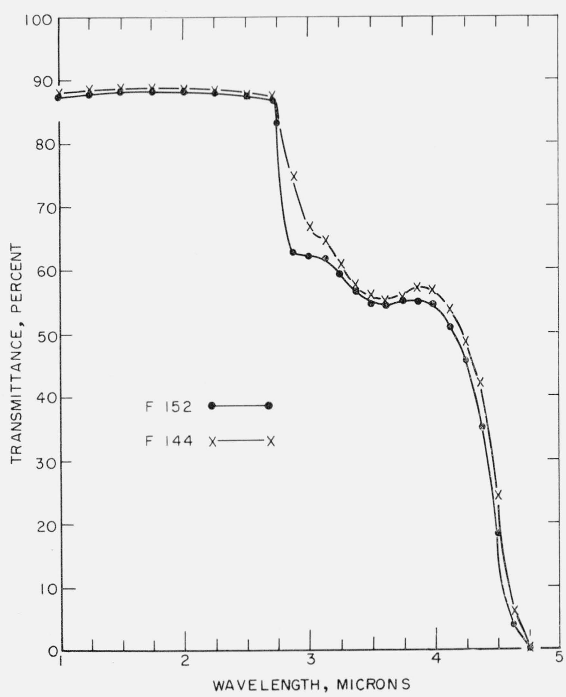

FIGURE 3. *Spectral transmittance of 2-mm thickness of two glasses containing 5 mole percent of* TiO_2.

See table 1 for compositions of glasses.

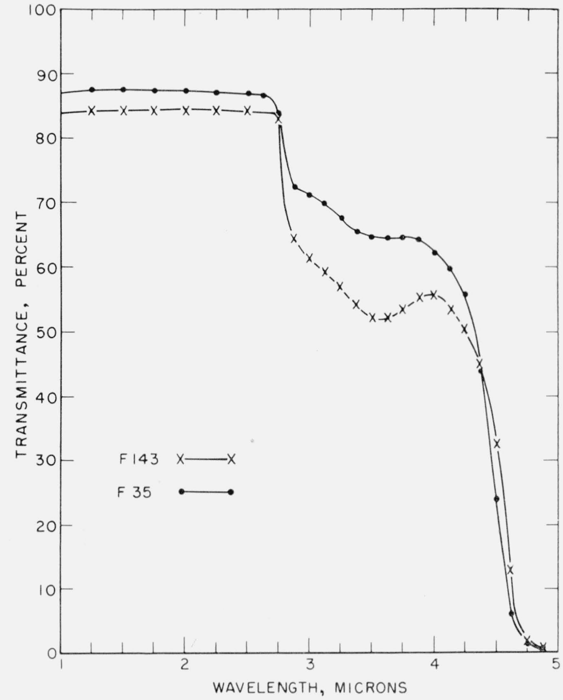

FIGURE 4. *Spectral transmittance of 2-mm thickness of two glasses containing 10 mole percent of* TiO_2.

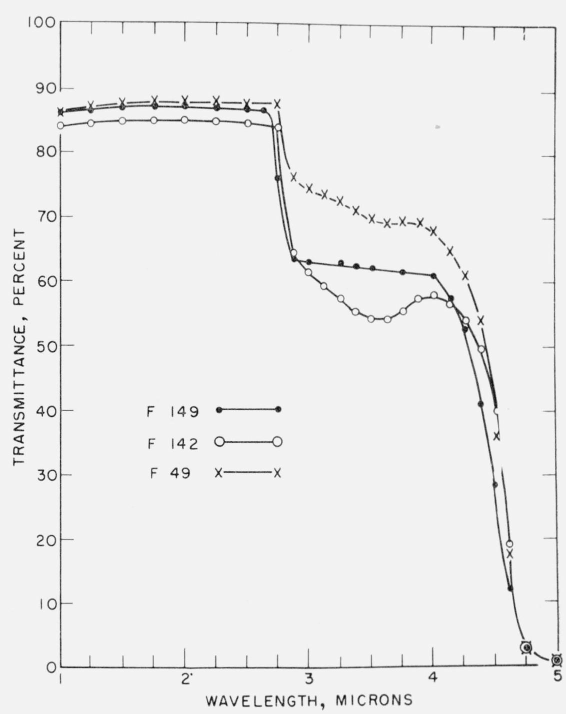

FIGURE 5. *Spectral transmittance of 2-mm thickness of three glasses containing 15 mole percent of* TiO_2.

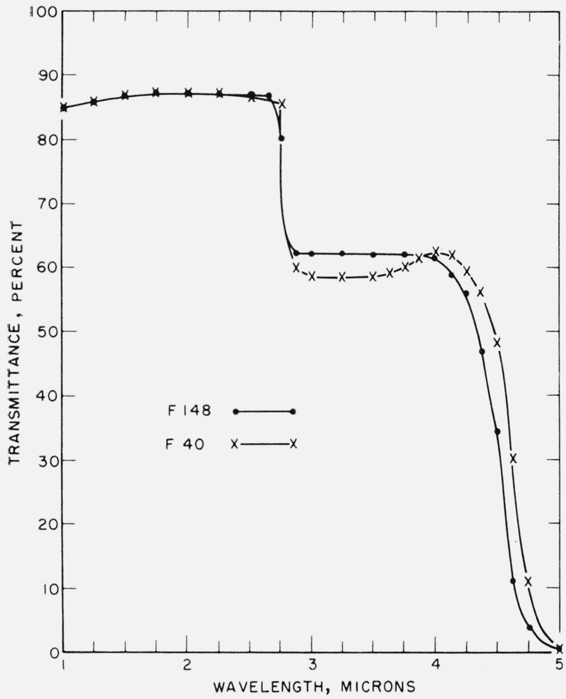

FIGURE 6. *Spectral transmittance of 2-mm thickness of two glasses containing 20 mole percent of* TiO_2.

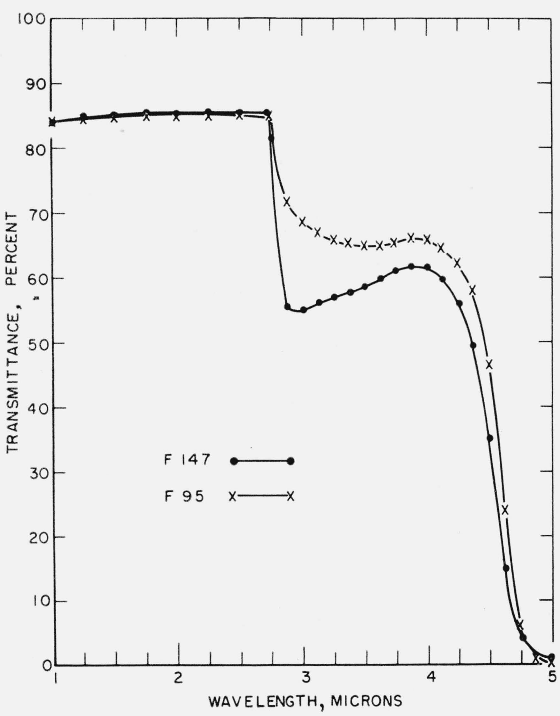

FIGURE 7. *Spectral transmittance of 2-mm thickness of two glasses containing 25 mole percent of* TiO_2.

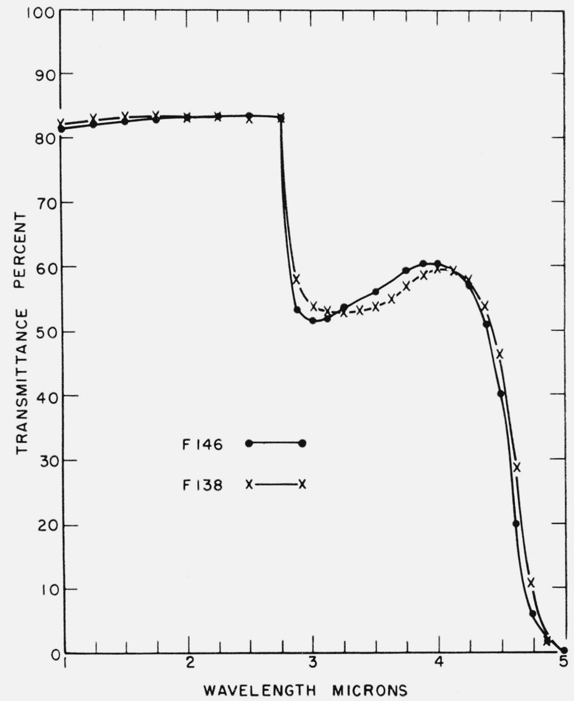

FIGURE 8. *Spectral transmittance of 2-mm thickness of two glasses containing 30 mole percent of* TiO_2.

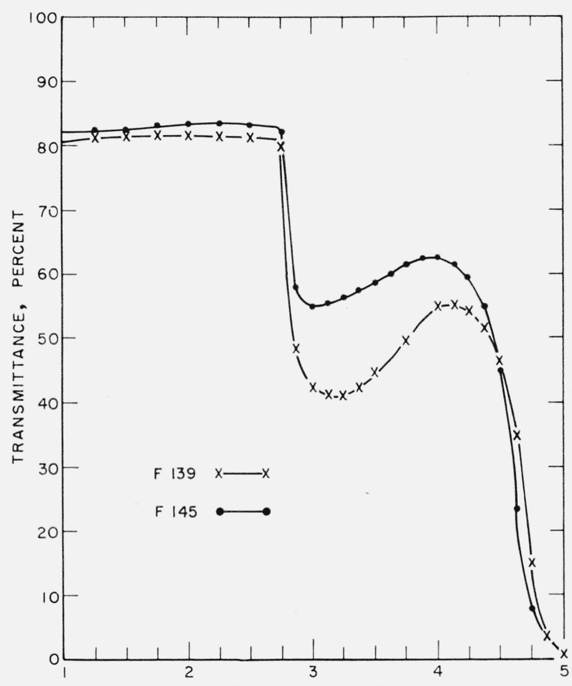

FIGURE 9. *Spectral transmittance of 2-mm thickness of two glasses containing 35 mole percent of* TiO_2.

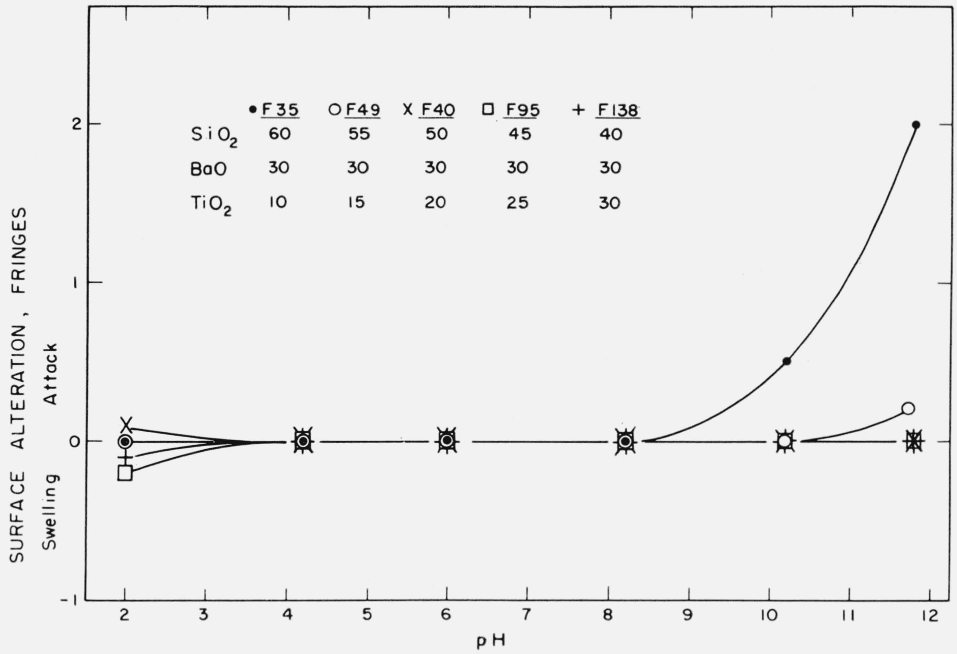

FIGURE 10. *Chemical durability of five* $BaO-TiO_2-SiO_2$ *glasses as a function of* pH.

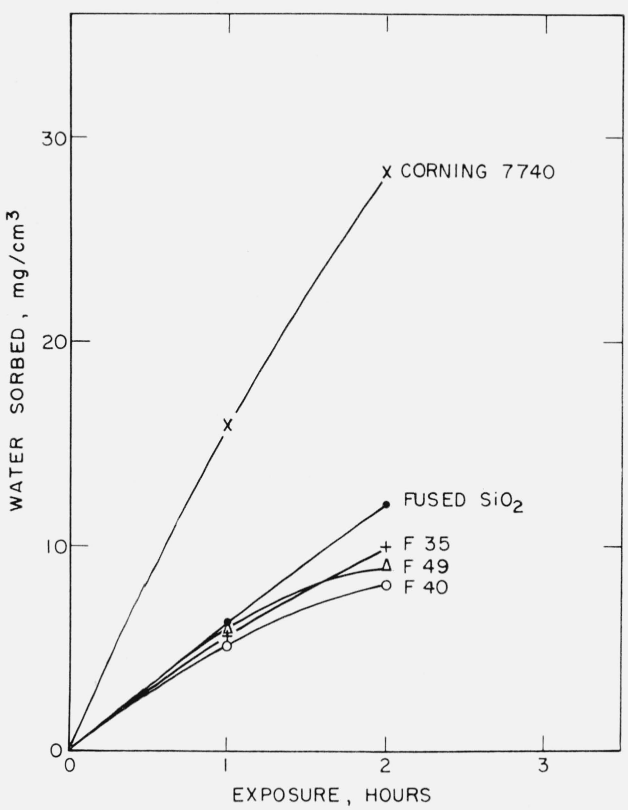

FIGURE 11. *Hygroscopicity of three* $BaO-TiO_2-SiO_2$ *glasses compared with Corning 7740 glass and fused* SiO_2.

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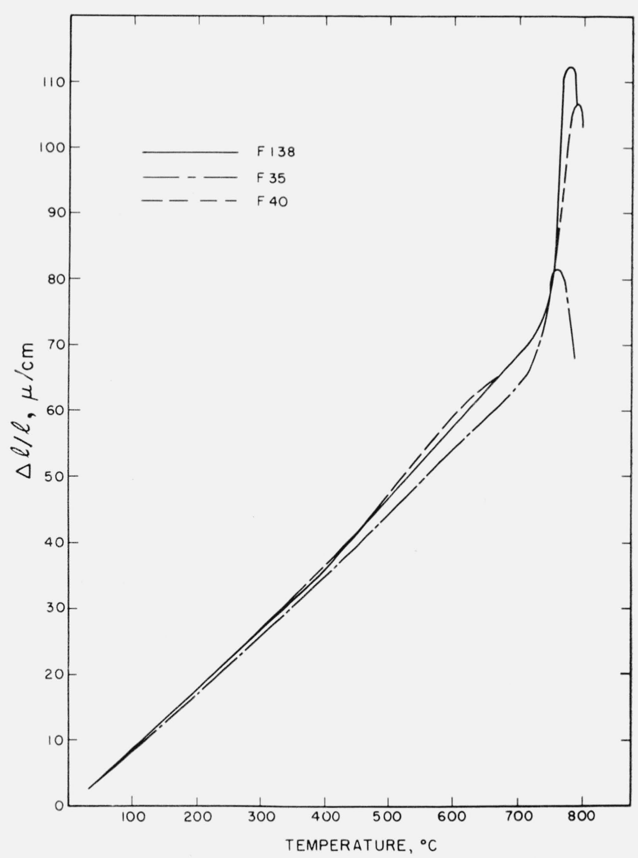

FIGURE 12. *Thermal expansion curves of three* $BaO-TiO_2-SiO_2$ *glasses as determined by an interferometric method.*