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Properties of Sodium Titanium Silicate Glasses [1]

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The glass-forming area of the Na_2O-TiO_2-SiO_2 system was surveyed. Glasses were made with refractive indices from 1.5184 to 1.8005, nu values from 51.5 to 23.2, and densities from 2.42 to 3.00. The glasses have higher dispersions and have considerably lower densities than the PbO glasses with comparable refractive indices.

1. Introduction

In order to give the optical designer greater freedom in his choice of glasses for use in optical devices there is a need for glasses that cover a considerable range of refractive indices, and for each index value, a range of dispersions. Most commercially available optical glasses having high refractive indices and high dispersions contain PbO in varying amounts. In general the refractive index and the dispersion increase with increasing PbO content. However, in PbO glasses there is a limiting value of dispersion for a given value of refractive index.

It has long been known that small additions of TiO_2 to a glass causes a relatively large increase in refractive index and dispersion. One of the early references to the use of TiO_2 in glass is that of Harcourt about 1870. He is reported to have produced "two 'nearly flawless' 3-inch disks of titanium glass and two of borate glass" [1].[2] The well-known work of Schott and Winkleman [2], in association with Abbe, the optical designer, was the first systematic attempt to determine the effect of chemical composition on the physical properties of glass. The immediate object of their work was the development of glasses having desirable optical properties. TiO_2 was one of the 28 oxides for which they studied the effects of composition on the physical properties of glass.

Colbert [3] has compared the effect of TiO_2 and PbO on the refractive indices of glasses. He added TiO_2 to a base glass of the composition $Na_2O,3SiO_2$ and PbO to a base glass of the same composition and found that in each series the refractive indices increased sharply.

Three series of glasses in the ternary system, Na_2O-TiO_2-SiO_2 were reported by Turnbull and Lawrence [4]. However, they did not survey the glass-forming area in the system. More recently Varguine [5] has reported on the glass-forming area of the Na_2O-TiO_2-SiO_2 system, but he gives data on only one series of glasses in the ternary system.

Thus, although studies have been made of glasses containing TiO_2, it was deemed desirable to make a systematic survey of the entire glass-forming region of the Na_2O-TiO_2-SiO_2 system, because it appeared that compositions in this ternary system could be used for the development of optical glasses having high refractive indices and high dispersions. Some of the properties of the glasses made in this survey are reported. The phase equilibrium diagram of the ternary system has not been determined, but information on the binary sides of the ternary system is available from previous work [6, 7, 8].

2. Experimental Procedure

The glasses were made in 500-g melts from batch materials of sufficient purity to satisfy the requirements for optical glass. The melts were made in platinum crucibles and stirred with a platinum–10 percent-rhodium stirrer. The melts were cast in the form of blocks approximately 3 by 3 by ¾ in. The details of the melting procedure are given in previous publications [9, 10]. The sag point [11] of each glass was used to establish an annealing temperature from which the glasses were cooled at 2½° C per hr to 350° C.

The liquidus temperature of each glass was determined by a temperature gradient method [12].

Refractive indices were determined on polished samples of the glasses in the form of 60° prisms for the C, D, F, and G′ lines by the NBS Optical Instrument Section.

The densities of the glasses were determined by the method described by Glaze, Young, and Finn [13].

The glasses were not analyzed. The compositions in table 1 are all calculated from batch.

3. Results

3.1. Glass-Forming Area of the Na_2O–TiO_2–SiO_2 System

The compositions of the melts are given in table 1 and are plotted in the triangular diagram of figure 1. Binary sodium silicate melts were made containing from 15 to 40 mole percent of Na_2O. The glass containing 15 mole percent of Na_2O devitrified during annealing and the other binary glasses developed a hazy appearance. The haziness of the annealed glasses increased with increasing SiO_2 content. Due to their hygroscopic nature none of the binary glasses could be polished in a water medium. This was also true of glasses containing 5 mole percent of TiO_2 and 25 or more mole percent of Na_2O. All the other ternary glasses containing 35 or more mole percent of Na_2O could be polished in a water medium but did not maintain a polished surface for more than a few weeks time.

[1] The work described in this report was sponsored by the Bureau of Ordnance, Department of the Navy.
[2] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Ternary* Na_2O-TiO_2-SiO_2 *compositions*

Melt	Na_2O	TiO_2	SiO_2	n_D	ν	ρ	Lquidus temperature	Primary phase [1]	Remarks
	Mole %	*Mole %*	*Mole %*				° *C*		
E1971	15	--------	85	--------	--------	2.335	--------	A	Devitrified in anneal.
E1972	20	--------	80	--------	--------	2.387	1105	A	Hygroscopic—could not polish.
E1973	25	--------	75	--------	--------	2.469	789	--------	Do.
E1974	30	--------	70	--------	--------	2.433	--------	--------	Do.
E1977	33.3	--------	66.7	--------	--------	2.489	874	--------	Do.
E1975	35	--------	65	--------	--------	2.499	--------	--------	Do.
E1976	40	--------	60	--------	--------	2.526	--------	--------	Do.
E1994	15	5	80	1.5184	51.5	2.429	>1220	A	Seedy.
E1995	20	5	75	1.5272	50.4	2.480	994	A	Do.
E1996	25	5	70	1.5318	49.7	2.512	--------	B	Seedy, hygroscopic.
E1967	30	5	65	--------	--------	2.533	798	B	Hygroscopic—could not polish.
E1968	35	5	60	--------	--------	2.567	--------	--------	Do.
E1969	40	5	55	--------	--------	2.590	--------	--------	Do.
E1970	45	5	50	--------	--------	2.607	--------	--------	Devitrified in anneal.
E1922	10	10	80	1.5481	43.5	2.439	>1260	A	Seedy—prism gave poor imagery.
E1999	12.5	10	77.5	1.5532	43.8	2.490	--------	--------	
E1960	15	10	75	1.5574	43.8	2.517	ca. 1200	A	
E2002	17.5	10	72.5	1.5618	43.7	2.546	1075	A	
E1961	20	10	70	1.5635	43.7	2.561	920	A	Striae.
E2003	22.5	10	67.5	1.5655	43.6	2.581	890	D	
E1907	25	10	65	1.5666	43.5	2.595	850	D	Hygroscopic.
E2000	27.5	10	62.5	1.5668	43.4	2.607	802	D	Do.
E1962	30	10	60	1.5672	43.2	2.615	806	B	Hygroscopic, striated.
E2001	32.5	10	57.5	1.5675	43.1	2.625	--------	--------	Hygroscopic.
E1908	35	10	55	1.5688	42.6	2.635	840	C	Do.
E1963	40	10	50	--------	--------	2.649	--------	--------	Hygroscopic—could not polish.
E1807	45	10	45	--------	--------	--------	--------	--------	Hygroscopic—surface devitrification.
E1795	50	10	40	--------	--------	--------	--------	--------	Devitrified in mold.
E1794	60	10	30	--------	--------	--------	--------	--------	Do.
E1959	12.5	12.5	75	1.5732	40.4	2.524	ca. 1300	A	
E1925	10	15	75	1.5868	36.4	2.520	>1260	A	Striated.
E1987	12.5	15	72.5	1.5936	37.3	2.565	--------	--------	Do.
E1926	15	15	70	1.5982	37.8	2.601	1099	A	Do.
E1988	17.5	15	67.5	1.6015	37.9	2.625	1024	A	
E1927	20	15	65	1.6019	38.2	2.641	845	D	
E2057	22.5	15	62.5	1.6015	38.4	2.655	--------	--------	
E1928	25	15	60	1.6016	38.5	2.668	883	D	
E2005	27.5	15	57.5	1.6015	38.6	2.678	765	D	
E1929	30	15	55	1.6006	38.6	2.684	840	E	Hygroscopic.
E1930	35	15	50	1.6007	38.2	2.696	905	E	Do.
E1931	40	15	45	1.6020	37.1	2.706	925	C	Do.
E1932	45	15	40	--------	--------	--------	1005	C	Hygroscopic—devitrified.
E1978	16.7	16.7	66.7	1.6147	36.1	2.645	1016	A	Striated.
E1914	23	17	60	1.6185	36.4	2.692	--------	--------	
E1938	10	20	70	1.6257	31.4	2.570	--------	--------	Index prism gave poor imagery.
E1989	12.5	20	67.5	1.6338	32.2	2.633	--------	--------	
E1980	15	20	65	1.6412	32.7	2.678	1090	--------	
E1990	17.5	20	62.5	1.6427	33.1	2.703	999	--------	Striated.
E1936	20	20	60	1.6424	33.5	2.712	928	--------	
E2007	22.5	20	57.5	1.6416	33.8	2.732	850	D	
E1909	25	20	55	1.6402	34.1	2.740	890	E	
E1986	30	20	50	1.6362	34.5	2.749	912	E	
E2009	32.5	20	47.5	1.6335	34.7	2.752	--------	--------	Hygroscopic.
E1910	35	20	45	1.6348	34.2	2.746	938	E	Do.
E1934	40	20	40	1.6358	33.3	2.750	906	E	Do.
E1809	45	20	35	--------	--------	--------	--------	--------	Devitrified in mold.
E1923	10	25	65	--------	--------	--------	>1275	--------	Contained devitrification.
E1942	15	25	60	1.6817	29.0	2.744	1185	--------	
E1991	17.5	25	57.5	1.6842	29.3	2.771	1110	F_2	
E1943	20	25	55	1.6837	29.7	2.789	1034	F_2	
E2010	22.5	25	52.5	1.6817	30.1	2.800	990	F_1	
E1889	25	25	50	1.6783	30.6	2.806	921	F_1	
E2011	27.5	25	47.5	1.6755	30.8	2.811	--------	--------	
E1890	30	25	45	1.6739	30.9	2.815	922	E	
E1891	35	25	40	1.6709	30.8	2.817	955	E	Hygroscopic.
E1924	10	30	60	--------	--------	--------	--------	--------	Devitrified.
E1944	15	30	55	1.7249	26.0	2.813	>1280	--------	
E1992	17.5	30	52.5	1.7267	26.4	2.839	1198	F_2	
E1945	20	30	50	1.7255	26.7	2.855	1106	F_1	
E2012	22.5	30	47.5	1.7228	27.1	2.866	1042	F_1	
E1946	25	30	45	1.7184	27.6	2.869	985	F_1	
E2013	27.5	30	42.5	1.7145	27.9	2.873	--------	--------	
E1947	30	30	40	1.7109	28.1	2.871	920	E	
E2014	32.5	30	37.5	1.7072	28.3	2.871	--------	--------	
E1948	35	30	35	1.7061	28.2	2.869	959	E	Hygroscopic.
E1804	40	30	30	--------	--------	--------	908	E	Devitrified in mold.
E2019	33.3	33.3	33.3	1.7304	26.7	2.914	970	E	
E1952	20	35	45	--------	--------	--------	1178	--------	Devitrified in mold.
E2025	22.5	35	42.5	1.7643	24.7	2.922	--------	--------	
E1983	25	35	40	1.7595	25.1	2.934	1038	F_1	
E2015	27.5	35	37.5	1.7530	25.5	2.934	--------	--------	
E1982	30	35	35	1.7496	25.7	2.932	960	F_1	
E2016	32.5	35	32.5	1.7437	26.0	2.920	--------	--------	
E1949	35	35	30	1.7413	26.0	2.926	952	E	Striated-hygroscopic.

See footnote at end of table.

TABLE 1. *Ternary* Na_2O-TiO_2-SiO_2 *compositions*—Continued

Melt	Na_2O	TiO_2	SiO_2	n_D	ν	ρ	Liquidus temperature	Primary phase [1]	Remarks
	Mole %	*Mole %*	*Mole %*				° *C*		
E1953	20	40	40	--------	--------	--------	--------	F_1	Devitrified in mold.
E2027	22.5	40	37.5	--------	--------	2.984	--------	--------	
E1954	25	40	35	1.8005	23.2	2.995	1060	F_1	Devitrified streaks in glass.
E1955	30	40	30	1.7874	23.9	2.988	1012	F_1	Stones.
E1956	35	40	25	--------	--------	--------	980	F_1	Devitrified in mold.
E1958	25	45	30	--------	--------	--------	1102	F_1	Devitrified in mold.
E1957	30	45	25	--------	--------	--------	1040	F_1	Do.
E1883	25	50	25	--------	--------	--------	--------	--------	Devitrified in mold.

[1] Primary phases: A=SiO_2; B=$Na_2Si_2O_5$; C=Na_2SiO_3; D=Unknown; E=$Na_2O \cdot TiO_2 \cdot SiO_2$; F_1=Unknown; F_2=Unknown.

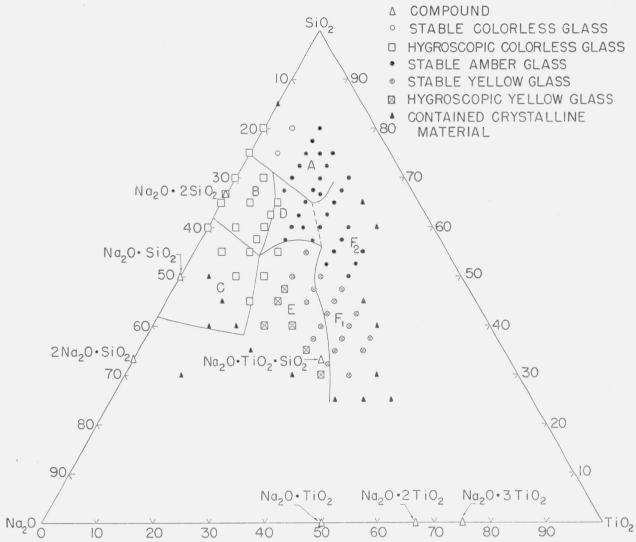

FIGURE 1. *Glass-forming area of the* Na_2O-TiO_2-SiO_2 *system*

Primary fields are: A, SiO_2; B, $Na_2O \cdot 2SiO_2$; C, $Na_2O \cdot SiO_2$; E, $Na_2O \cdot TiO_2 \cdot SiO_2$; D, F_1 and F_2, unidentified.

All of the ternary glasses containing 5 mole percent and some containing 10 and 15 percent of TiO_2 were practically colorless except when viewed edgewise. The remainder of the ternary glasses were either amber or yellow in color. As the Na_2O/SiO_2 ratio is increased, the amount of color in the glasses decreases rapidly, so that glasses are obtained whose color compares favorably with PbO glasses having comparable optical properties. The composition ranges of the hygroscopic, amber, and yellow glasses are indicated in figure 1.

3.2. Liquidus Temperatures

The liquidus temperatures of many of the glasses are given in table 1 and plotted in figure 2. The letters under the curves indicate the primary phases at the liquidus. The letters, A, B, C, and E stand for SiO_2, $Na_2O \cdot 2SiO_2$, $Na_2O \cdot SiO_2$, and $Na_2O \cdot TiO_2 \cdot SiO_2$, respectively. The compositions of the primary phases designated D, F_1, and F_2 were not determined. The approximate composition ranges of the primary fields are indicated, insofar as they are known, in figure 1. A region designated F_2 is located adjacent to the D and F_1 primary fields. The approximate boundaries of this field, if it is a primary field, are not known. In the F_2 field adjacent to the D field

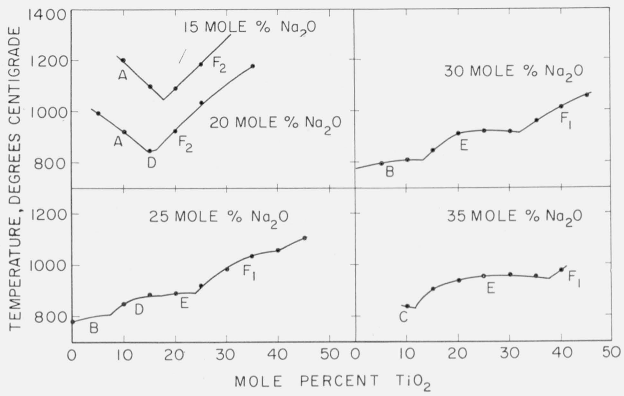

FIGURE 2. *Liquidus temperatures of glasses in five series of* Na_2O-TiO_2-SiO_2 *glasses.*

Primary phases present at the liquidus are: A, SiO_2; B, $Na_2O \cdot 2SiO_2$; C, $Na_2O \cdot SiO_2$; E, $Na_2O \cdot TiO_2 \cdot SiO_2$; D, F_1 and F_2 were not identified.

the crystals appearing at the liquidus and from 20 to 50 degrees below the liquidus, are too small to permit the determination of their properties by microscopic means. At lower temperatures phase D is observed, but it is believed that the submicroscopic crystals are not phase D. Adjacent to the phase F_1 field crystals with the same appearance and properties with the exception of refractive indices as phase F_1, were observed.

The properties of the crystals from phases D, E, and F_1 are:

Phase D. Composition unknown. Thick rods with high birefringence, n_{max} about 1.70 and n_{min} about 1.60.

Phase E. Composition believed to be $Na_2O \cdot TiO_2 \cdot SiO_2$. Rod-shaped crystals with low birefringence, parallel extinction, negative elongation. n_{max} about 1.77 and n_{min} about 1.73.

Phase F_1. Composition unknown. Needle-shaped crystals with moderate birefringence, parallel extinction, positive elongation, n_{max} about 2.00, and n_{min} below 2.00.

3.3. Refractive Indices and Dispersions

Glasses were obtained with refractive indices from 1.5184 to 1.8005 and nu values [3] from 51.5 to 23.2.

[3] Nu value, ν, is defined as:

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

The refractive indices of the glasses are plotted in figure 3. The lines connect glasses containing equal moles of TiO_2. No simple relation is readily evident between refractive indices and increase in Na_2O content of the glasses.

The nu values of the glasses are plotted in figure 4. As in the case of the refractive index curves of figure 3, the nu value curves change slope and direction as the TiO_2 content of the glasses is increased.

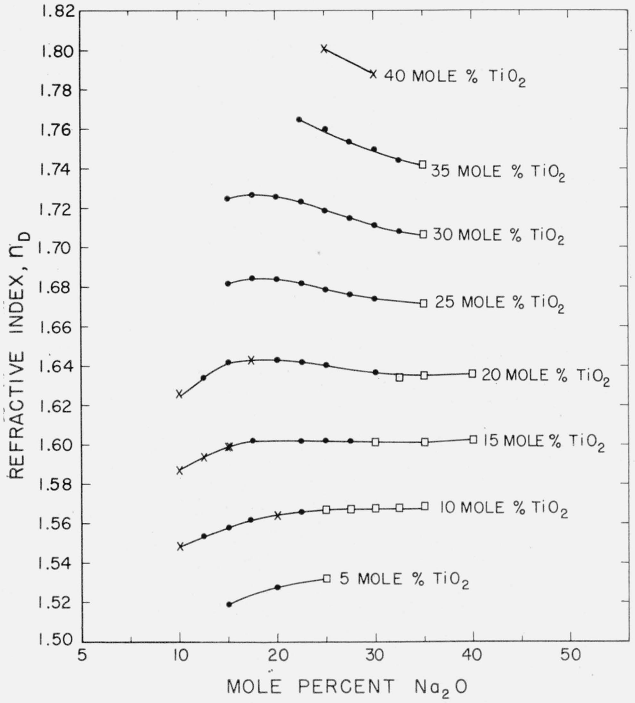

FIGURE 3. *Refractive indices of the* Na_2O-TiO_2-SiO_2 *glasses.*
Glasses which contained striae are identified by × and hygroscopic glasses by □.

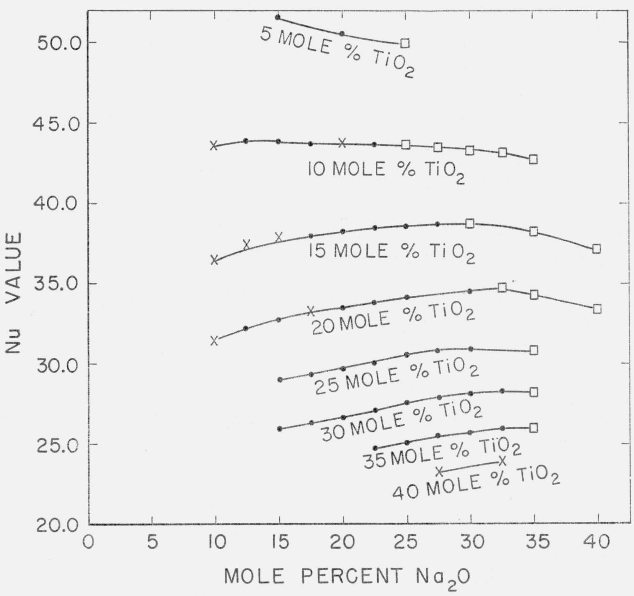

FIGURE 4. *Nu values of the* Na_2O-TiO_2-SiO_2 *glasses.*
Glasses which contained striae are identified by × and hygroscopic glasses by □.

In figure 5, the optical properties of typical optical flint glasses [14] and some of the Na_2O-TiO_2-SiO_2 glasses are compared. All of the curves for the experimental glasses seem to parallel each other. The glasses containing 25 and 30 mole percent of Na_2O all plot on the same line. Typical optical flint glasses with refractive indices above 1.605 have lower dispersions (higher nu values) than the Na_2O-TiO_2-SiO_2 glasses with corresponding refractive indices.

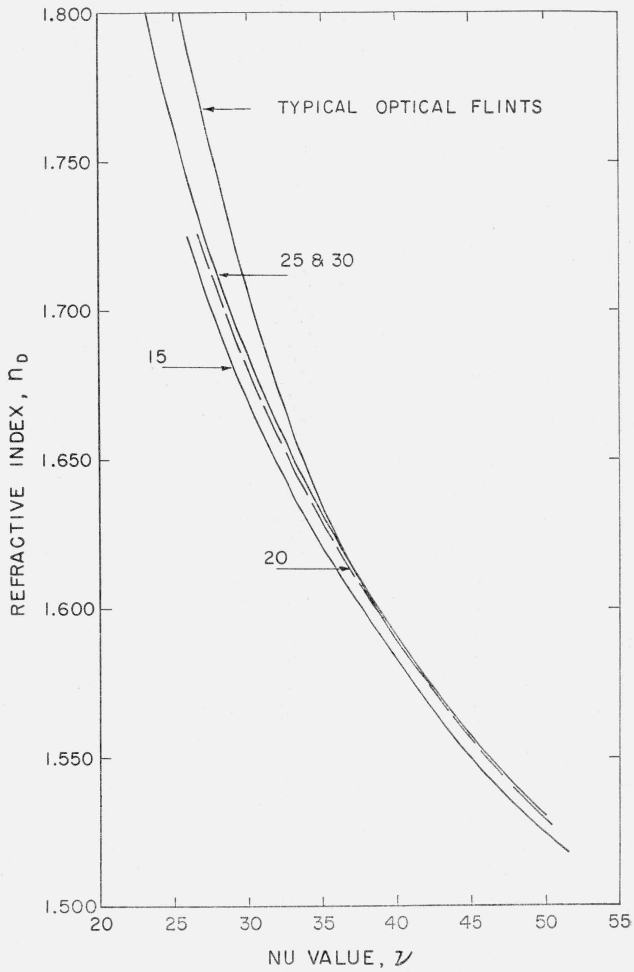

FIGURE 5. *Refractive indices versus nu values of* Na_2O-TiO_2-SiO_2 *and typical optical flint glasses.*
The numbers 15, 20, 25, and 30 indicate the mole percent of Na_2O in the Na_2O-TiO_2-SiO_2 glasses plotted on the respective curves.

3.4. Densities

The densities of the glasses containing TiO_2 are considerably lower than for PbO glasses with the same indices of refraction. The density of the TiO_2 glasses range from 2.42 to 3.00 while the density of the PbO glasses cover the range of 3.0 to 5.0. For this reason the less dense TiO_2 glasses may be of interest in applications where weight is a factor of prime importance.

The densities of the glasses are plotted in figure 6. There is a definite increase in density from series to series as TiO_2 is increased. As Na_2O is increased in

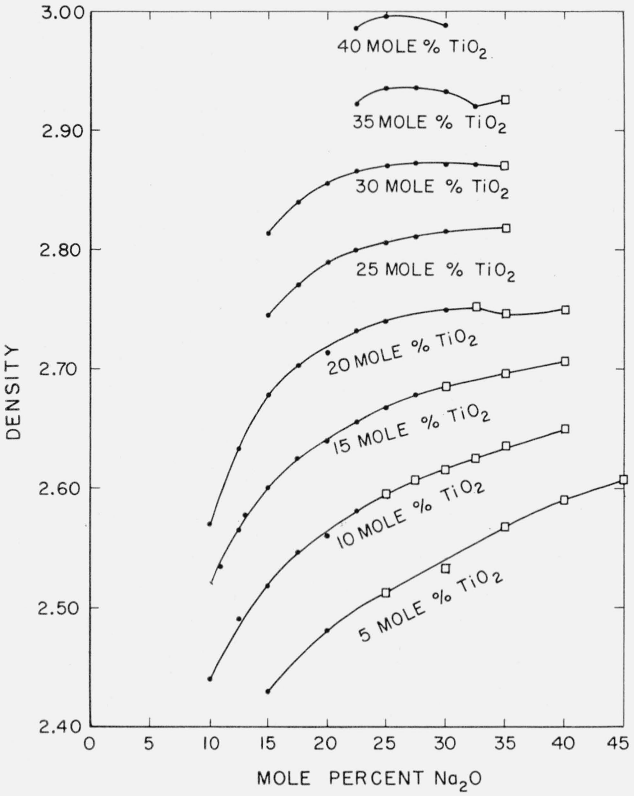

FIGURE 6. *Densities of* Na_2O-TiO_2-SiO_2 *glasses.*

Hygroscopic glasses are indicated by □.

each series of constant TiO_2 content, the density of the glasses containing less than 30 mole percent of TiO_2 increase. However, the amount of change in density per unit change in composition is not constant. An exception to this observation is the hygroscopic glasses containing 20 mole percent of TiO_2, but the values of density of these glasses may be affected by absorbed moisture.

3.5. Spectral Transmittances

The spectral transmittances of the glasses containing 25 mole percent of TiO_2 are plotted in figure 7. The ultraviolet absorption edge shifts toward the visible with increase in SiO_2 content. The sharpness of the absorption edge decreases with increase in color. In figure 8 the spectral transmittances of the glasses containing 25 mole percent of Na_2O are plotted. The absorption edge shifts to longer wavelengths with increase in TiO_2 content of the glasses. In the case of two glasses with visible yellow color the absorption edge not only shifts with increase in TiO_2, but it is not as sharp as for the colorless glasses. This is also evident in figure 9 where the sharpness of the absorption edge decreases with increase in color of the glass. The glasses are listed in figures 7, 8, and 9 in the order of increasing visible color.[4]

[4] It is recognized that some of the glass color may be due to the presence of impurities such as iron or platinum. The iron contents of the batch materials, calculated as Fe_2O_3 are: sand, 0.006 percent; soda ash, 0.001 percent; and TiO_2, 0.001 to 0.01 percent. The amount of platinum would depend on the corrosiveness of the individual melts on the platinum crucible, and no data is available. The heat treatment of the glasses is another factor which could affect the color.

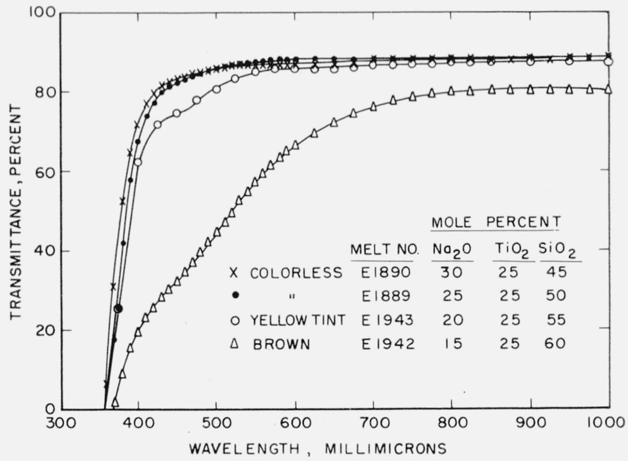

FIGURE 7. *Spectral transmittances of some* Na_2O-TiO_2-SiO_2 *glasses containing 25 mole percent of* TiO_2.

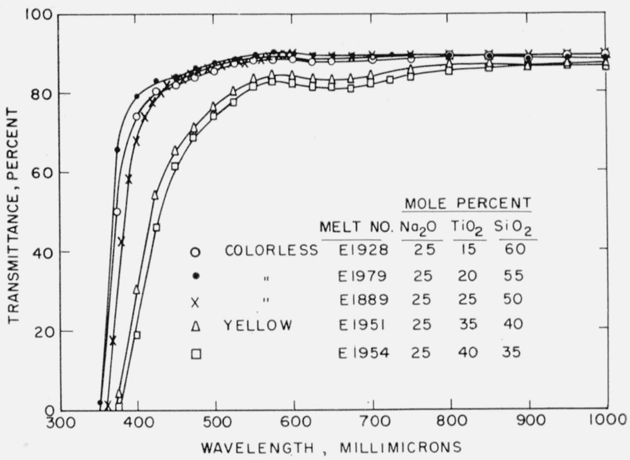

FIGURE 8. *Spectral transmittances of some* Na_2O-TiO_2-SiO_2 *glasses containing 25 mole percent of* Na_2O.

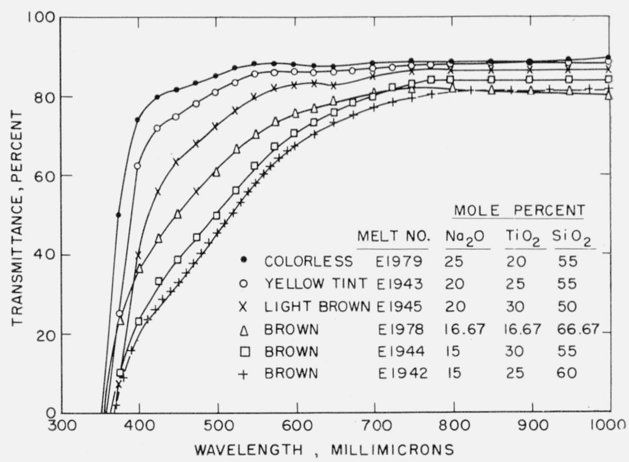

FIGURE 9. *Spectral transmittances of some* Na_2O-TiO_2-SiO_2 *glasses with increasing color.*

4. Summary

The glass-forming region of the Na_2O-TiO_2-SiO_2 system was surveyed. Glasses were made with refractive indices from 1.5184 to 1.8005, nu values from 51.5 to 23.2, and densities from 2.42 to 3.00. The glasses have considerably lower densities than PbO glasses with comparable optical properties. Over a limited composition range the color of TiO_2 glasses compares favorably with that of PbO glasses of comparable optical properties.

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