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Part I

HIGH STRENGTH - HIGH MODULUS GLASS FIBERS

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FOREWORD

This report was prepared by the Glass Research Laboratory of Owens-Corning Fiberglas Corporation, Granville, Ohio under USAF Contract AF 33(615)-1370. This contract was initiated under Project No.7320, "Fibrous Materials for Decelerators and Structures" , Task No. 732001, "Nonmetallic and Composite Materials" and Project No. 7340," Organic and Inorganic Fibers", Task No. 734003, "Structural Plastic and Composite Materials". This report covers the work accomplished during the period March 1964 through February 1965.

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This technical documentary report has been reviewed and is approved.

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ABSTRACT

The results of the present investigation have shown that glass fibers drawn from compositions located in the SiO_2-Al_2O_3-ZnO system posses tensile strengths in excess of 800,000 psi. Glass fibers drawn from compositions in the SiO_2-Al_2O_3-MgO system have given similar results, particularly at fiber diameters in the 0.00015 to 0.00020 inch range.

The modulus of elasticity of glass fibers obtained from compositions located in the SiO_2-Al_2O_3-MgO system can be increased to 16.0×10^6 psi. This is accomplished by lowering the fiber diameter to the 0.00015 to 0.00020 inch range.

In the SiO_2-Al_2O_3-Na_2O system, the fiber forming temperature, the tensile strength and the modulus of elasticity change with composition in a manner which gives a break in the composition vs. property curves at the point where the Al to Na ratio is 1. This is related to the change in the coordination number of the aluminum at this ratio which has been proposed in the literature.

The properties measured for glasses in the SiO_2-TiO_2-K_2O system do not appear to lead to as clear a concept of glass structure. Properties vary gradually with composition, with no evidence of a sharp break at any point. There is some indication that the rate of change of properties is dominated more by the silica content than is the case in the SiO_2-Al_2O_3-Na_2O system.

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I

HIGH STRENGTH - HIGH MODULUS GLASS FIBERS

INTRODUCTION

The present study was undertaken for the purpose of preparing and studying glass compositions which would produce glass fibers possessing high tensile strengths and high moduli of elasticity. An additional study was initiated which sought to establish a relationship between tensile strength and the composition and probable constitution of selected glasses. Results of this additional study are presented separately under the title "Relationship Between Composition and Properties of Selected Glasses."

Emphasis in the study of high strength - high modulus glass fibers was placed on glasses of two general classifications. In the first classification, SiO_2-Al_2O_3-R_xO glasses were prepared in which the alumina to R_xO ratio was maintained at one on a mol basis. In the second classification, SiO_2-Al_2O_3-R_xO glasses were prepared in which the alumina to R_xO ratio varied from 0.5 to 2.0. The R_xO component included the alkali and alkaline earth oxides. Other modifications of both classifications were made using several other glass formers and modifiers.

The study initially proceeded with the preparation of glass compositions in the SiO_2-Al_2O_3-MgO system, notably S-994 and related glasses. Subsequent studies were then made by substituting alkali and alkaline earth oxides for all or part of the MgO in the base SiO_2-Al_2O_3-MgO glasses.

II

DISCUSSION

A. Study of SiO_2-Al_2O_3-R_xO Glasses

1. Glass Preparation, Fiberization, and Testing

Each glass composition was prepared by dry mixing the appropriate end member materials which were of at least U.S.P. grade. The dry batch was melted in precious metal crucibles. Temperatures used were 2900°F for two hours and 3200°F for an additional hour or 2900°F for 24 hours. Both methods gave equivalent results. Each batch was removed from its crucible and remixed at least once during the melting operation. All glasses were cooled by plunging the hot crucible directly from the furnace into a cold water bath. Fibers were obtained from each glass composition by remelting the prepared cullet in a one-hole precious metal bushing capable of reaching temperatures in excess of 3200°F.

To test the fibers, virgin filaments were captured by hand in the usual manner and, to determine tensile strength, were wound on a stainless steel fork. Each fork normally contained 6-8 fiber lengths for study after this operation. The apparatus for measuring tensile strength was designed to test one fiber at a time, recording essentially the load elongation diagram for each fiber. The fibers were loaded by a screw-driven cross-head at a constant rate of strain of 0.25 in./in./minute applied to a 2 inch gage length of fiber. The load cell consisted of a catilever beam with a linear variable differential tranformer (LVDT) as the displacement sensing element. The load cell was calibrated by dead weight loading. The LVDT was powered by a strain gage amplifier. The signals from the LVDT were first rectified through matched pairs of germanium diodes, then passed through gain and zero potentiometers and recorded on a single channel recorder (Esterline-Angus).

The fiber diameter of each fiber length (6-8 measurements) was determined from a short length of fiber remaining on the fork after mounting. The fibers were mounted on a microscope slide in a liquid of appropriate index of refraction and their diameters measured under a 430 power microscope with the aid of a micrometer eyepiece.

The modulus of elasticity of a particular glass composition was determined by direct measurement of the elongation of an unannealed fiber under load. In most cases, these fibers had diameters of approximately 0.00060 to 0.00080.

2. Tensile Strength and Modulus of Elasticity Results

a. Glasses located in the SiO_2-Al_2O_3-MgO system were studied extensively. The composition locations are shown in Figure 1, which represents the phase diagram of this system and shows the boundaries between primary phase fields as straight lines. The compositions studied are located at the circled points. The theoretical glass compositions studied in the system are shown

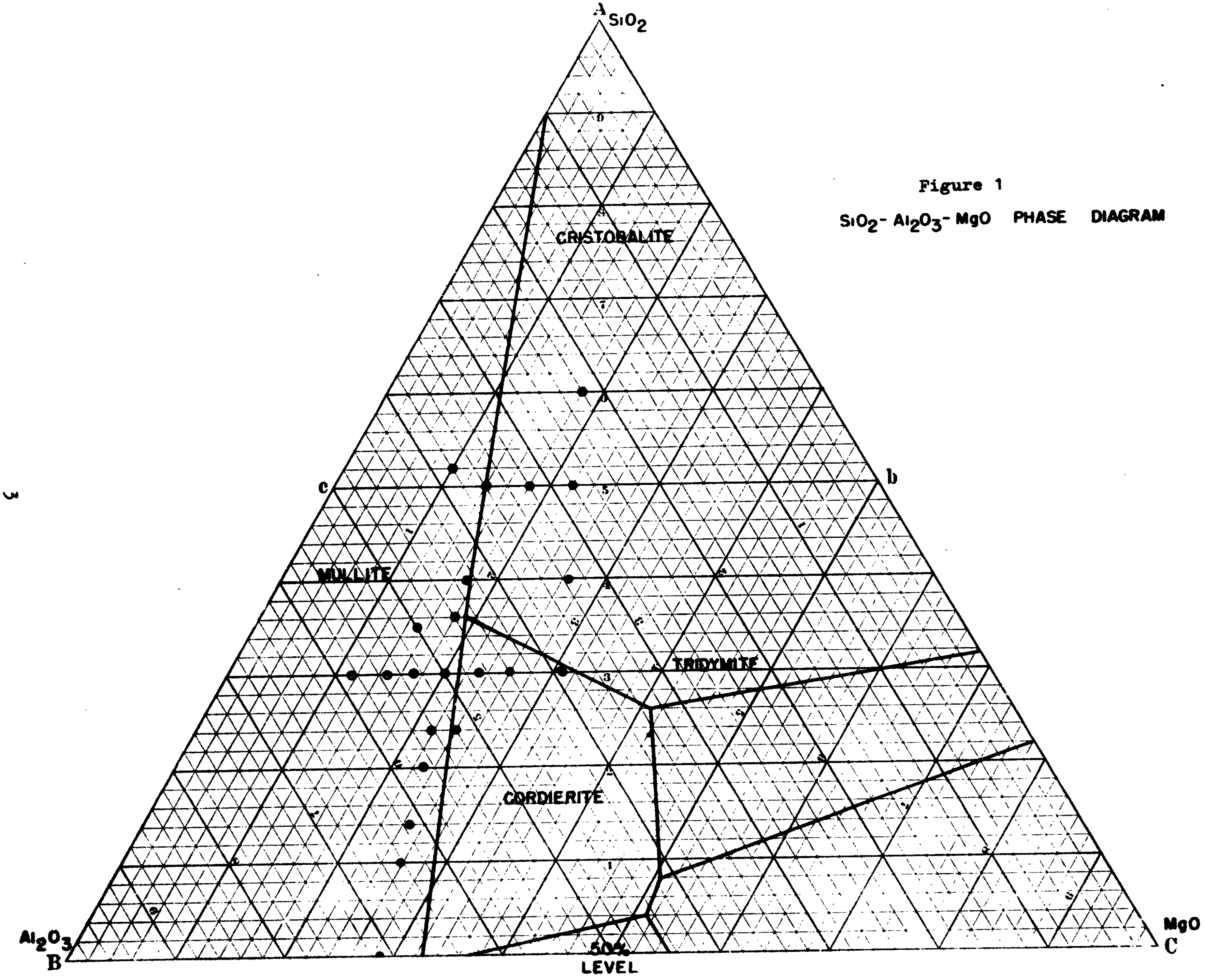


Figure 1

SiO_2- Al_2O_3- MgO PHASE DIAGRAM

TABLE I

THEORETICAL GLASS COMPOSITIONS AND FIBER PROPERTIES

GLASS NO.	OXIDES (a. weight % - b. mol %)									AVERAGE TENSILE STRENGTH x 10^3psi	MODULUS x 10^6psi	AVERAGE DIAMETER x 10^{-5}in.	FORMING TEMP. ^oF	NO. OF FIBERS
	SiO_2	Al_2O_3	MgO	Li_2O	K_2O	BeO	CaO	ZnO	SrO	BaO				
X-994	a.65.0 b.68.68	25.0 15.56	10.0 15.76								700-600	12.5	16-35	2750	16
X-1751	a.65.0 b.67.7	23.5 14.4	11.5 17.8								674	11.6	31	2700	21
X-1753	a.65.0 b.67.0	22.0 13.3	13.0 19.9								671	12.4	42	2700	20
X-1755	a.65.0 b.69.8	26.4 16.6	8.6 13.7								716	12.0	40	2800	20
X-1757	a.65.0 b.70.5	27.7 17.7	7.3 11.8								678	12.7	35	2850	21
X-1758	a.68.0 b.71.6	23.0 14.2	9.0 14.2								692	12.5	40	2790	21
X-1759	a.70.0 b.73.5	21.5 13.3	8.5 13.3								699	12.6	37	2800	19
X-1760	a.62.0 b.66.0	27.2 17.0	10.8 17.0								834	13.6	32	2700	18
X-1761	a.60.0 b.64.0	28.7 18.0	11.3 18.0								678	12.3	22	27.50	15
X-1762	a.65.0 b.63.9	19.6 12.1	15.4 24.1								600	11.6	37	2600	21
X-1763	a.65.0 b.71.6	29.2 18.9	5.8 9.5								698	12.7	42	2910	19
X-1888	a.55.0 b.59.1	32.3 20.5	12.7 20.4								395	12.3	35	2735	17

TABLE I (Continued)

GLASS NO.	OXIDES (a. weight % - b. mol %)										AVERAGE TENSILE STRENGTH	MODULUS	AVERAGE DIAMETER	FORMING TEMP.	NO. OF
	SiO_2	Al_2O_3	MgO	Li_2O	K_2O	BeO	CaO	ZnO	SrO	BaO	x 10^3psi	x 10^6psi	x 10^{-5}in.	°F.	FIBERS
X-1889	a.57.0 b.61.0	30.8 19.4	12.2 19.5								431	12.0	35	2735	16
X-1890	a.50.0 b.54.2	35.9 22.9	14.2 22.9								COULD NOT BE FIBERIZED				
X-1898	a.70.0 b.70.3	16.8 9.9	13.2 19.8								676	11.7	30	2950	6
X-1899	a.75.0 b.75.3	14.0 8.3	11.0 16.5								619	11.1	33	2850	18
X-1900	a.80.0 b.80.2	11.2 6.6	8.8 13.2								651	11.3	33	3145	14
X-1901	a.76.0 b.80.3	19.0 11.8	5.0 7.9								505	-	28	3155	13
X-1902	a.67.5 b.71.8	25.0 15.7	7.5 12.5								726	11.7	16	2915	18
X-1903	a.62.0 b.65.1	26.0 16.1	12.0 18.8								519	12.4	33	2700	17
X-1657	a.75.0 b.78.1	18.0 11.0	7.0 10.9								662	11.5	31	3060	15
X-1659	a.75.0 b.76.6	16.0 9.6	9.0 13.7								716	11.7	32	3170	12
X-1764	a.65.0 b.67.1	27.1 16.5		7.9 16.4							601	10.0	44	2720	21
X-1765	a.65.0 b.64.4	24.3 14.2		10.7 21.4							COULD NOT BE FIBERIZED				
X-1767	a.65.0 b.69.4	29.3 18.4		5.7 12.2							615	10.8	39	2800	21

TABLE I (Continued)

GLASS NO.		OXIDES (a. weight % - b. mol %)										AVERAGE TENSILE STRENGTH x 10^3psi	MODULUS x 10^6psi	AVERAGE DIAMETER x 10^{-5}in.	FORMING TEMP. °F.	NO. OF FIBERS
		SiO_2	Al_2O_3	MgO	Li_2O	K_2O	BeO	CaO	ZnO	SrO	BaO					
X-1768	a.	65.0	30.6		4.4							641	11.0	34	2900	20
	b.	70.7	19.6		9.7											
X-1769	a.	68.0	24.8		7.2							600	10.0	37	2760	20
	b.	70.0	15.0		15.0											
X-1770	a.	70.0	23.2		6.6							COULD NOT BE FIBERIZED				
	b.	71.9	14.0		14.1											
X-1765	a.	62.0	29.4		6.6							546	10.4	33	2710	21
	b.	64.2	17.9		17.9											
X-1786	a.	60.0	31.0		9.0							337	9.9	49	2640	21
	b.	62.2	18.9		18.8											
X-1795	a.	65.0	18.2			16.8						COULD NOT BE FIBERIZED				
	b.	75.2	12.4			12.4										
X-1796	a.	65.0	12.3			22.7						347	7.9	36	2850	19
	b.	74.9	8.4			16.7										
X-1797	a.	70.0	15.6			14.4						COULD NOT BE FIBERIZED				
	b.	79.2	10.4			10.4										
X-1798	a.	80.0	10.4			9.6						COULD NOT BE FIBERIZED				
	b.	86.6	6.6			6.8										
X-1799	a.	65.0	22.6					12.4				486	12.0	24	2750	12
	b.	71.0	14.6					14.5								
X-1800	a.	65.0	16.7					18.3				456	12.5	49	2660	19
	b.	68.8	10.4					20.7								
X-1820	a.	65.0	27.4					7.6				583	11.3	38	2940	21
	b.	72.8	18.1					9.1								
X-1821	a.	70.0	19.4					10.7				598	10.2	35	2810	20
	b.	75.4	12.3					12.4								

TABLE I (Continued)

GLASS NO.		OXIDES (a. weight % - b. mol %)									AVERAGE TENSILE STRENGTH	MODULUS	AVERAGE DIAMETER	FORMING TEMP	NO. OF
	SiO_2	Al_2O_3	MgO	Li_2O	K_2O	BeO	CaO	ZnO	SrO	BaO	x 10^3psi	x 10^6psi	x 10^{-5}in.	°F.	FIBERS
X-1822	a.80.0 b.84.0	12.9 8.0					7.1 6.0				COULD NOT BE FIBERIZED				
X-1823	a.60.0 b.66.4	25.8 16.8					14.2 16.8				571	11.4	42	2720	19
X-1792	a.65.0 b.74.0	19.5 13.1						15.5 13.0			626	11.3	41	3115	17
X-1792 (1)	a.56.9 b.68.6	22.9 15.7						18.2 15.7			630	11.8	27	2915	17
X-1792 (2)	a.59.0 b.68.68	22.7 15.56						18.3 15.76			815	11.5	26	2915	11
X-1793	a.75.0 b.82.1	13.9 8.9						11.1 8.9			COULD NOT BE FIBERIZED				
X-1824	a.65.0 b.76.0	17.4 12.0							17.6 12.0		432	11.4	40	2900	18
X-1825	a.65.0 b.76.0	11.6 8.0							23.5 16.0		355	13.7	29	2900	18
X-1826	a.65.0 b.76.0	23.2 16.0							11.8 8.0		COULD NOT BE FIBERIZED				
X-1827	a.60.0 b.71.9	19.8 14.0							20.2 14.1		568	11.3	37	2850	20
X-1828	a.70.0 b.80.0	14.9 10.0							15.1 10.0		COULD NOT BE FIBERIZED				
X-1829	a.80.0 b.87.3	9.9 6.4							10.1 6.4		COULD NOT BE FIBERIZED				
X-1830	a.65.0 b.79.8	14.0 10.1								21.0 10.1	393		45	3200	7

TABLE I (Continued)

GLASS NO.		OXIDES (a. weight % - b. mol %) SiO_2	Al_2O_3	MgO	Li_2O	Na_2O	K_2O	BeO	CaO	ZnO	SrO	BaO	AVERAGE TENSILE STRENGTH x 10^3psi	MODULUS x 10^6psi	AVERAGE DIAMETER x 10^{-5}in.	FORMING TEMP. °F.	NO. OF FIBERS
X-1831	a.	65.0	8.8									26.3	226	8.7	31	3115	16
	b.	80.7	6.4									12.8					
X-1851	a.	65.0	28.1					6.9					682	13.7	37	3000	16
	b.	66.3	16.8					16.9									
X-1852	a.	65.0	23.5					11.5					327	14.0	34	3050	12
	b.	61.1	13.0					26.0									
X-1891	a.	70.0	24.1					5.9					635	13.2	39	3025	17
	b.	71.2	14.4					14.4									
X-1835	a.	65.8	24.4	5.1	3.7								407	12.1	38	2735	17
	b.	68.7	15.6	7.9	7.9												
X-1836	a.	63.3	24.4	4.9		7.5							532	11.0	40	2850	15
	b.	68.7	15.6	7.9		7.9											
X-1837	a.	60.9	23.5	4.7			11.0						413	10.6	42	2955	17
	b.	68.7	15.6	7.9			7.4										
X-1838	a.	63.7	24.5	4.9					6.8				604	12.6	40	2795	17
	b.	68.7	15.6	7.9					7.9								
X-1839	a.	61.8	23.8	4.8						9.6			542	12.9	39	2955	16
	b.	68.7	15.6	7.9						7.9							
X-1840	a.	60.2	23.2	4.6							11.9		391	11.7	43	2900	18
	b.	68.7	15.6	7.9							7.9						
X-1641	a.	57.0	21.9	4.4								16.7	485	-	44	2900	16
	b.	68.7	15.6	7.9								7.9					
X-1896	a.	66.2	25.5	5.1				3.2					638	12.4	33	2850	16
	b.	68.6	15.6	7.9				7.9									
X-1897	a.	71.7	13.8	11.0				3.4					504	11.7	33	2795	16
	b.	68.6	7.8	15.8				7.8									

TABLE I (Continued)

GLASS NO.		OXIDES (a. weight % - b. mol %) SiO$_2$	Al$_2$O$_3$	MgO	P$_2$O$_5$	TiO$_2$	ZrO$_2$	HfO$_2$	GeO$_2$	AVERAGE TENSILE STRENGTH x 10^{3}psi	MODULUS x 10^{6}psi	AVERAGE DIAMETER x 10^{-5}in.	FORMING TEMP. °F.	NO. OF FIBERS
X-1842	a. b.	65.0 71.8	18.0 11.6	7.0 11.7	10.0 4.9					488	11.6	38	2950	18
X-1843	a. b.	60.0 68.6	18.0 12.1	7.0 12.0	15.0 7.3					357	11.4	35	2900	16
X-1844	a. b.	55.0 65.1	18.0 12.5	7.0 12.4	20.0 10.0					COULD	NOT BE	FIBERIZED		
X-1845	a. b.	55.0 61.9	25.0 16.6	10.0 16.8	10.0 4.7					580	11.8	29	2900	14
X-1849	a. b.	64.0 68.1	25.0 15.7	10.0 15.8	1.0 0.4					554	12.0	34	2850	18
X-1850	a. b.	60.0 65.4	25.0 16.1	10.0 16.3	5.0 2.3					406	11.4	38	2735	17
X-1856	a. b.	50.0 58.1	25.0 17.3	10.0 17.1	15.0 7.4					494	11.7	46	2900	20
X-1846	a. b.	60.0 64.2	25.0 15.8	10.0 15.9		5.0 4.1				361	12.0	39	2735	16
X-1847	a. b.	55.0 59.7	25.0 16.0	10.0 16.2		10.0 8.2				260		32	2700	15
X-1848	a. b.	63.0 66.9	25.0 15.6	10.0 15.8		2.0 1.6				393	12.3	34	2775	16
X-1853	a. b.	64.5 68.3	25.0 15.6	10.0 15.8			0.5 0.3			620	11.6	35	2735	20
X-1654	a. b.	64.0 68.0	25.0 15.6	10.0 15.8			1.0 0.5			626	12.1	35	2735	17
X-1855	a. b.	64.0 69.1	22.2 14.1	8.8 14.1			5.0 2.7			585	12.5	34	2795	17

TABLE I (Continued)

GLASS NO.	OXIDES (a. weight % - b. mol %) SiO$_2$	Al$_2$O$_3$	MgO	P$_2$O$_5$	TiO$_2$	ZrO$_2$	HfO$_2$	GeO$_2$	AVERAGE TENSILE STRENGTH x 10^{3}psi	MODULUS x 10^{6}psi	AVERAGE DIAMETER x 10^{-5}in.	FORMING TEMP. ^{o}F.	NO. OF FIBERS
X-1657	a. 62.0	25	10			3			511	13.5	31	2770	17
	b. 66.6	15.8	16.0			1.5							
X-1858	a. 60.0	25	10			5			524	12.1	-	2750	21
	b. 65.1	16.0	16.2			2.7							
X-1659	a. 63.0	19.4	7.6			10.0			615	12.8	39	2975	18
	b. 69.5	12.6	12.5			5.4							
X-1893	a. 62.0	17.9	7.1			13.0			429	11.6	51	3100	20
	b. 69.3	11.8	11.8			7.1							
X-1894	a. 65.0	17.9	7.1			10.0			457	11.7	37	3100	20
	b. 71.4	11.6	11.6			5.3							
X-1887	a. 64	25	10				1		501	12.0	26	2955	17
	b. 68.1	15.7	15.9				0.3						
X-1860	a. 64.0	25.0	10.0					1	477	12.7	43	3095	14
	b. 67.9	15.6	15.8					0.6					
X-1685	a. 60.0	25.0	10.0					5.0	506	12.2	32	2850	21
	b. 64.8	15.9	16.0					3.1					
X-1886	a. 55.0	25.0	10.0					10.0	467	12.6	39	2850	19
	b. 60.8	16.3	16.4					6.4					

in Table 1, which also lists pertinent physical properties for each glass. On Table 1, see glass numbers X-994, X-1751 through X-1763, X-1888 through X-1890, X-1898 through X-1903, X-1657 and X-1659.

Most of the data presented describes glass compositions with either constant weight percentages of SiO_2 and variable Al_2O_3 to MgO ratios or constant Al_2O_3 to MgO ratios and variable weight percentages of SiO_2. These data are summarized graphically in Figures 2 and 3.

Figure 2 indicates that at a constant SiO_2 content of 65% by weight, the tensile strength of the series of compositions increases with an increasing Al_2O_3 to MgO ratio. The increase continues until a maximum is reached at an Al_2O_3 to MgO ratio of 1. At this point it is postulated that additional Al_2O_3 enters sixfold coordination in the glass structure.(1) The data show a reverse change in slope at this point in the curve, which indicates such a structural change is possible and does take place. Increasingly higher forming temperatures and much greater devitrification tendencies above the Al_2O_3 to MgO ratio of 1.0 also make it difficult to interpret the data obtained, but there is a good indication that beyond 1.5 mol % the tensile strength is beginning to increase again at a lower rate.

Tensile strength results for X-994 as listed in Table 1 show a range of values. It is felt that these results are indicative of the structural sensitivity of the glass at this point (Al_2O_3/MgO = 1.0). Strength values for other glasses at this ratio have shown similar variability and reinforce the view that slight changes in composition produce fairly large changes in strength.

The modulus values plotted in Figure 2 show no clear-cut trend. There appears to be an over-all increase in modulus with increasing Al_2O_3 to MgO ratio.

Figure 3 indicates that at a constant Al_2O_3 to MgO ratio of 1.0 and a variable SiO_2 content by weight the tensile strength of the series of compositions increases with an increase in the SiO_2 content. The increase is continuous up to a SiO_2 level of from 60-65% where the tensile strength begins to drop again. Again increased forming temperatures and greater devitrification tendencies are found at the higher SiO_2 levels. The plotted value beyond 70% by weight SiO_2 may therefore not be entirely correct.

The high tensile strength peak for X-1760 and the range of values for X-994 are again indicative of the composition sensitivity of these glasses at this point.

The modulus values appear to follow the trend established by the strength values, with maximum values located in the 60-70% SiO_2 range.

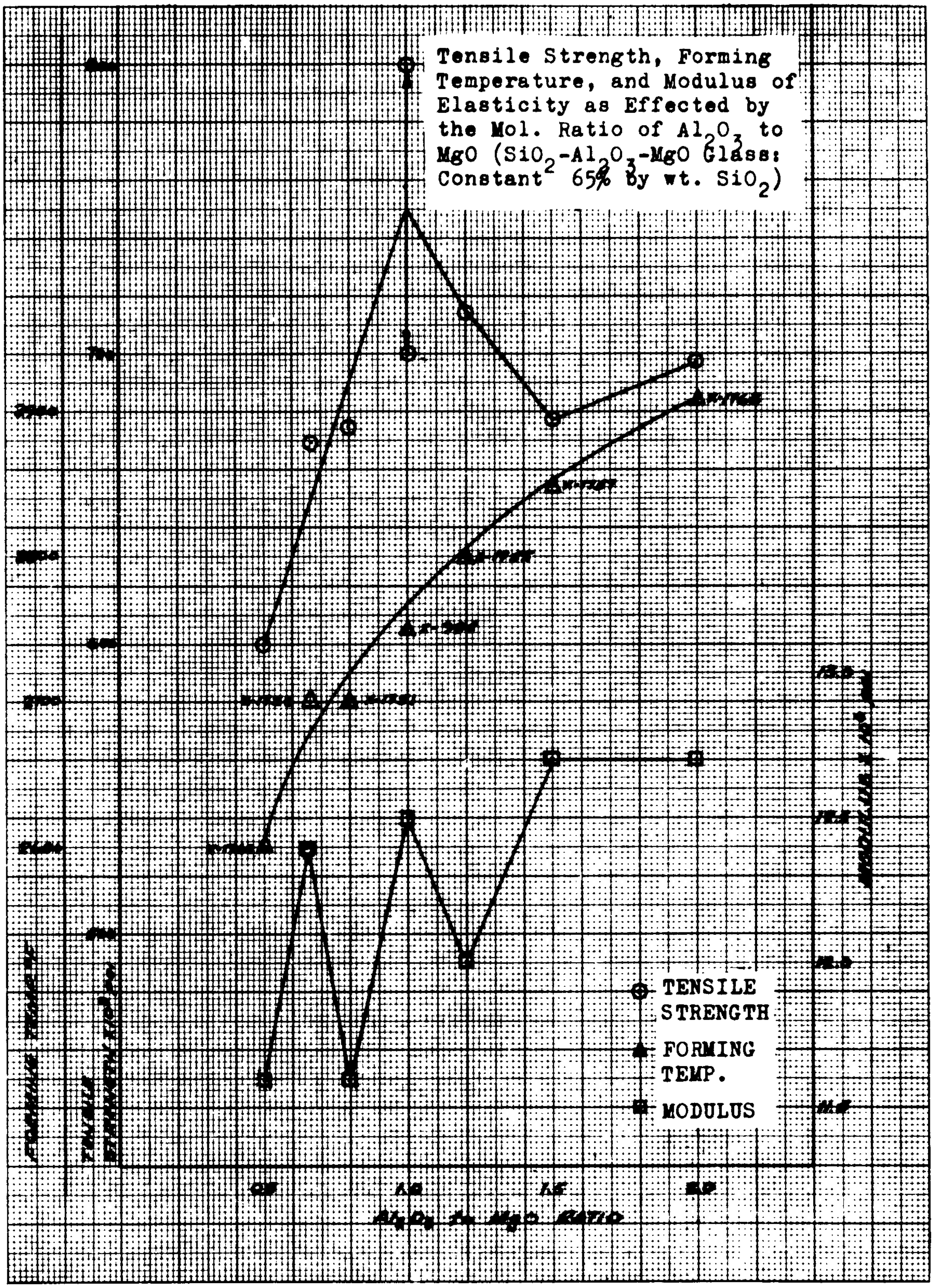


FIGURE 2 Tensile Strength, Forming Temperature, and Modulus as Effected bu the Mol Ratio of Al_2O_3 to MgO

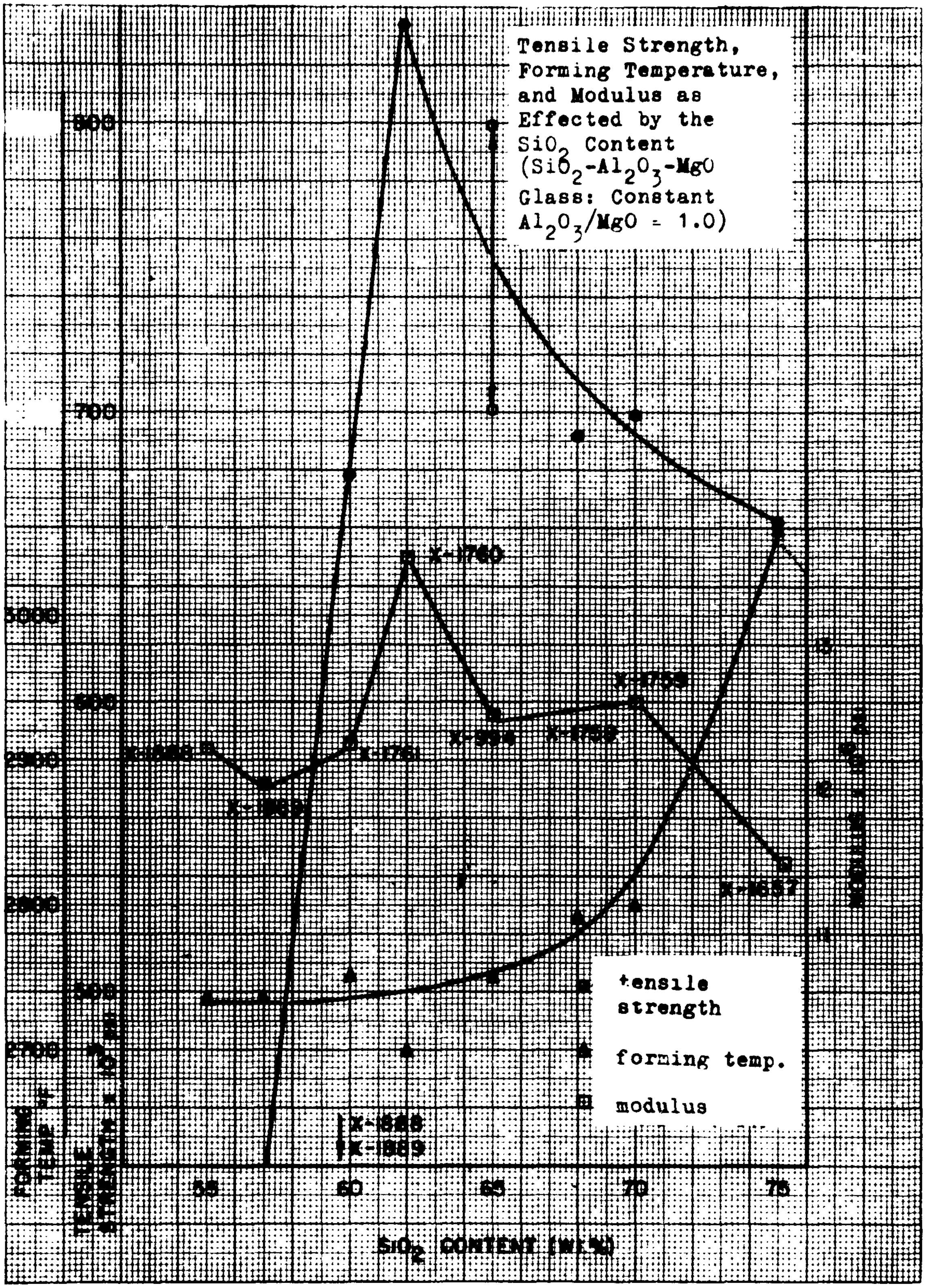


FIGURE 3 Tensile Strength, Forming Temperature, and Modulus as Effected by the SiO_2 Content

The tensile strength values of the remaining glasses which are not plotted tend to point out the trends established in Figures 2 and 3. These are as follows:

(1) The glasses with the best forming characteristics and highest tensile strengths are located at an approximate Al_2O_3 to MgO ratio of approximately 1.0 and at a SiO_2 level ranging from 60-70% by weight.

(2) Glasses with Al_2O_3 to MgO ratios much less than 1.0 do not have desirable tensile strengths.

(3) Glasses with Al_2O_3 to MgO ratios much greater than 1.0 do not have high strengths because of fiberization difficulties and greater devitrification tendencies.

(4) Glasses within the desirable composition limits (1) have tensile strength values which are sensitive to slight structural changes because of the changes in coordination of the Al^{+++} ion in this area. It is therefore postulated that there is a structural link between the coordination of the Al^{+++} ion in the glass and the tensile strength and modulus of filaments made from the glass.

b. SiO_2-Al_2O_3-R_xO Compositions

Table 1 lists the theoretical compositions and properties of a series of glasses containing SiO_2, Al_2O_3, and R_xO (where R_xO is Li_2O, K_2O, BeO, CaO, ZnO, SrO, or BaO.) Attention is directed to glasses numbered X-1764 through X-1770, X-1785 and X-1786, X-1795 through X-1796, X-1799 and X-1800, X-1820 through X-1823, X-1824 through X-1831, X-1851 and X-1852, and X-1891 through X-1893.

Figure 4 summarizes the properties of fibers produced from these glasses. The highest average strength and modulus value in each series of compositions has been compared to the range of values established for the SiO_2-Al_2O_3-MgO series. The tensile strength values plotted for the alkali oxide substitutions show a continuous strength decreases in going from MgO to Li_2O to K_2O. A similar decreases occurs in the modulus values. It is postulated that the Li^+ ion causes a reduction because its valence is only one and it has a much lower field strength than Mg^{++}. Similarly, the K^+ ion has a valence of only one, has an even lower field strength than Li^+, and has an ionic radius about twice as large as Mg^{++}.

The alkaline earth oxide substitutions for MgO show a continuous decreases in strength. Ranking the alkaline earth ions by ionic size and field strength may help account for the trend in the tensile strength.

Ion	Ionic Size	Field Strength
Be^{++}	0.31	16.7
Mg^{++}	0.65	4.5
Zn^{++}	0.74	3.6
Ca^{++}	0.99	2.0
Sr^{++}	1.13	1.6
Ba^{++}	1.35	1.1

The Zn^{++} ion, though not an alkaline earth ion, is included to show its similarity to Mg^{++}. It would thus be expected to act like Mg^{++}. This is the case, as shown in Figure 4, at least for tensile strength values.

With such a trend established, it would be expected that a SiO_2-Al_2O_3-BeO glass would show outstanding strength properties. There is some indication that such may be the case, but no final values are yet available. Glasses of this type have enhanced devitrification and phase separation tendencies, which would be explained by the extremely high field strength of Be^{++}. Currently, such tendencies have made fiberization of good quality fibers difficult.

The plot of modulus of elasticity values for the alkaline earth oxide substitutions show a variable pattern. The BeO addition produces the best results, with SrO, surprisingly, a close second. Unfortunately, the high modulus values do not correspond to the strongest glasses in the series.

Summarizing the results of the study in which alkali oxides and alkaline earth oxides were substituted for MgO in the SiO_2-Al_2O_3-MgO series of glasses, it should be noted that:

(1) The substitution of ZnO for MgO produced the only glasses with tensile strength values comparable to those in the SiO_2-Al_2O_3-MgO system.

(2) When substituting alkali oxides for MgO, the tensile strength decreased as the size of the ion increased.

(3) When substituting alkaline earth oxides for MgO, the tensile strength decreased as the size of the ion increased. The effect of BeO has not yet been definitely determined and should not be included in this conclusion.

(4) None of the oxide substitutions for MgO improved the modulus of elasticity above that associated with glasses in the SiO_2-Al_2O_3-MgO system, except for the BeO substitution.

This is attributed to the small size and high field strength of the Be^{++} ion.

C. SiO_2-Al_2O_3-MgO-R_xO Compositions

Table 1 lists the theoretical compositions and properties of a series of glasses based on the X-994 composition where R_xO

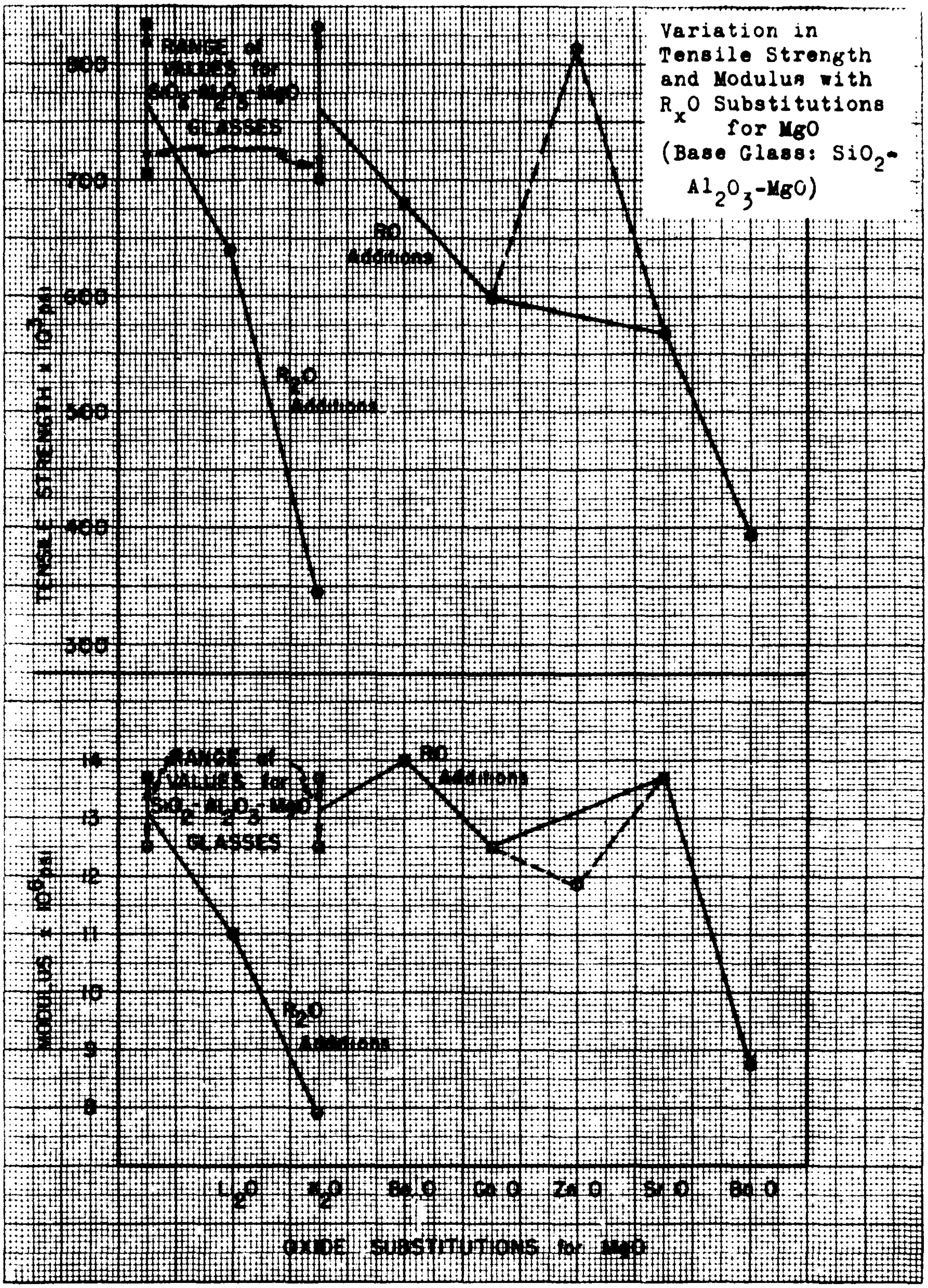


FIGURE 4 Variation in Tensile Strength and Modulus with R_xO Substitutions for MgO

component is substituted for half the MgO on a mol basis. (R_xO = Li_2O, Na_2O, K_2O, BeO, CaO, ZnO, SrO, BaO.) Attention is directed to glasses numbered X-1835 through X-1841 and X-1896.

Figure 5 summarizes the property data. The value of tensile strength and modulus for each oxide addition is compared to the range of values established for the SiO_2-Al_2O_3-MgO glass series. No trend is evident except to note that all of the additions tend to reduce the tensile strength of the SiO_2-Al_2O_3-MgO series of glasses. The trend of the modulus curve cannot be explained, except to note that the glasses with higher modulus values do not correspond to those with high tensile strengths, except in the case of the SiO_2-Al_2O_3-MgO-BeO glass.

2. SiO_2-Al_2O_3-MgO Glasses with Additions of Other Glass Formers and Intermediates

Table 1 lists the theoretical compositions and properties of a series of glasses containing SiO_2-Al_2O_3-MgO and one other glass forming or intermediate oxide (P_2O_5, TiO_2, ZrO_2, HfO_2, or GeO_2). On Table 1 see the following glass numbers:

Glasses containing P_2O_5 - X-1842 through X-1845, X-1849 through X-1850, and X-1856.

Glasses containing TiO_2 -X-1846 through X-1848.

Glasses containing ZrO_2 - X-1853 through X-1855, X-1857 through X-1859, X-1893 through X-1894

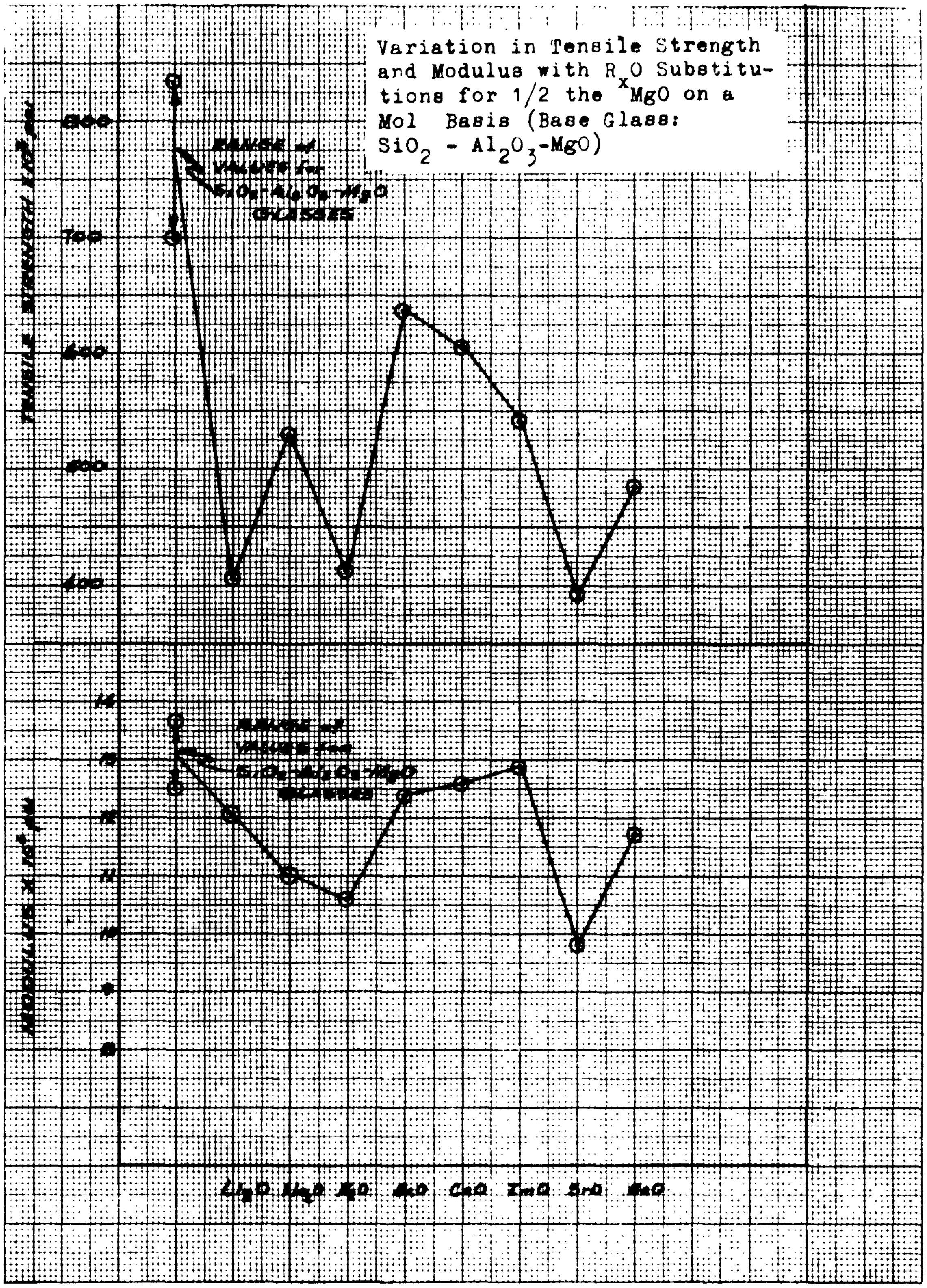
Glasses containing HfO_2 - X-1867

Glasses containing GeO_2 - X-1860, X-1885, X-1886

The X-994 composition was used as the base glass. In general, the added oxide was either substituted for part of the SiO_2 content of the X-994 composition or for part of the SiO_2, Al_2O_3, and MgO content on a weight basis. In all cases the mol ratio of Al_2O_3 to MgO remained approximately equal to 1.

A systematic study of the exact effect of each addition on the tensile strength of the base glass was not attempted. In general, however, the tensile strength results indicate that the addition of P_2O_5 for a portion of the SiO_2 resulted in a general strength decrease as the P_2O_5 content increased. An even greater strength drop resulted when P_2O_5 was substituted for a portion of the SiO_2, Al_2O_3, and MgO. Modulus values were not greatly affected by any of the additions and cannot be explained.

TiO_2 substitutions for part of the SiO_2 caused the greatest drop in strength of all the additions used. The strength decreased as the TiO_2 content increased. Again, modulus values were not greatly affected and this response cannot be explained.



Variation in Tensile Strength and Modulus with R_xO Substitutions for 1/2 the MgO on a Mol Basis (Base Glass: SiO_2 - Al_2O_3-MgO)

FIGURE 5 Variation in Tensile Strength and Modulus with R_xO Substitutions for 1/2 the MgO on a Mol Basis

Interpretation of the data for the glasses containing ZrO_2 is difficult. However, it appears that small ZrO_2 additions improve modulus values slightly. Even such small additions, however, decrease tensile strength. HfO_2 has the same effect.

Finally, the addition of GeO_2 for part of the SiO_2 greatly reduces the tensile strength below that associated with X-994. Modulus does not seem to be affected, but again no explanation is offered.

3. The Effect of Fiber Diameter on Tensile Strength and Modulus of Elasticity

Preliminary results from several studies of the forming parameters associated with the fiberization of SiO_2-Al_2O_3-MgO glasses have indicated that tensile strength and modulus properties were improved when the diameter of fibers under test was reduced. The tensile strength of virgin X-994 fiber is normally 700-725,000 psi for a 0.00040 inch diameter fiber. This figure is apparently raised to 800-850,000 psi for a fiber with an apparent diameter of 0.00015 to 0.00020 inch. Since there are problems encountered with accurately measuring fibers of this diameter with the micrometer eyepiece, further work in this area is warranted.

Modulus of elasticity values are also apparently improved for lower diameter fibers. The following modulus measurements have been made:

Glass	Modulus x 10^6 psi	Method Employed	Measured Diameter
X-994	12.4	Elongation	0.00065 in.
X-994	13.4	Elongation	0.00031
X-994	13.6	Sonic	0.00027
X-994	16.0	Elongation	0.00018

Note the modulus value, measured by the sonic method, of a fiber with a diameter of 0.00027 inches. The sonic method does not require a diameter measurement. This finding reinforces the view that the lower diameter fibers do have improved moduli. Further work in this area is definitely desirable.

Glasses in systems other than the SiO_2-Al_2O_3-MgO series have been checked to determine the effect of reductions in fiber diameter on both tensile strength and modulus. The properties of glasses in the SiO_2-Al_2O_3-Li_2O and SiO_2-Al_2O_3-CaO systems did not change with reductions in fiber diameter. Improved properties were evident, however, in the SiO_2-Al_2O_3-ZnO system.

B. Relationship Between Composition and Properties of Selected Glasses

1. General

Glass fibers with the highest possible tensile strength and modulus of elasticity are desired for many important applications. These properties are intimately related to the ultimate structure of glass. Knowledge of the structure of a glass and its relationship these properties is invaluable in developing new glass compositions with superior performance.

The work reported here was undertaken to provide some insight into the relationship between glass structure and the properties of tensile strength and modulus of elasticity. In papers by Day and Rindone(1,2), it has been shown that a number of physical properties of certain glasses in the SiO_2-Al_2O_3-Na_2O field vary in a systematic manner with composition changes. Further, composition vs. property curves usually showed breaks which were related to proposed changes in glass structure. It was found that in a set of related compositions in which the Al to Na ratio varied, a break occurred at the point where this ratio was one. It was postulated that at ratios below one, the aluminum was in fourfold coordination and participated in the glass network, while at higher ratios some of the aluminum assumed sixfold coordination. This proposition was based in part upon the total number of oxygen ions available. At Al to Na ratios less than one, there are less than two. The work reported here started as an attempt to find out whether modulus of elasticity and tensile strength of fibers could be related to glass composition and presumably structure in the same manner as had been done with other properties.

Considerable property data have also been published for glasses in the SiO_2-TiO_2-K_2O system(3). These glasses were also reported to show deviations in curves of properties vs. composition which were tentatively related to changes in coordination number of the titanium from six to eight. These observations, plus the superficial similarity between the two systems, led to the extension of the work by including a study of this composition field also.

The SiO_2-Al_2O_3-K_2O system is an attractive one for further study, inasmuch as it differs from each of the previously studied systems by only one constituent. It may be possible to relate the two through study of this system.

Experimental Procedure

a. SiO_2-Al_2O_3-Na_2O System

(1) Compositions Studied

Table II gives the compositions in mol percentages for all glasses studied. The glasses are divided into five related series. Series II and IV comprise sets of compositions similar to those given the same designation in the papers by Day and Rindone(1,2). In general, all glasses in each series contain the same percentage of silica. The exception is Series IV in which all components vary simultaneously.

(2) Preparation and Testing of Specimens

Batches compounded from relatively pure commercial raw materials were melted in crucibles to form the glass used to

TABLE I

COMPOSITIONS IN MOL PER CENT
SiO_2-Al_2O_3-Na_2O SYSTEM

Series II

	X-1580A	X-1585A	X-1586A	X-1587A	X-1588A	X-1589A	X-1590A
SiO_2	75.00	75.00	75.00	75.00	75.00	75.00	75.00
Al_2O_3	-	3.13	6.25	9.38	12.50	15.00	16.25
Na_2O	25.00	21.88	18.75	15.63	12.50	10.00	8.75
Al/Na	0	.14	.33	.60	1.00	1.50	1.86

Series IV

	X-1580A	X-1591B	X-1592B	X-1593A	X-1594A	X-1595A
SiO_2	75.00	71.43	66.67	65.52	64.29	62.96
Al_2O_3	-	7.14	16.67	18.97	21.43	24.07
Na_2O	25.00	21.43	16.67	15.52	14.29	12.96
Al/Na	0	.33	1.00	1.22	1.50	1.86

Series V

	X-1866	X-1867	X-1868	X-1869	X-1870	X-1871	X-1961
SiO_2	65.97	65.97	65.97	65.97	65.97	65.97	65.97
Al_2O_3	-	6.00	12.00	17.00	20.00	22.00	24.00
Na_2O	34.03	28.03	22.03	17.03	14.03	12.03	10.03
Al/Na	0	.21	.55	1.00	1.43	1.83	2.40

Series VI

	X-1877	X-1878	X-1879	X-1970	X-1971	X-1880	X-1972
SiO_2	57.00	57.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	-	6.00	12.00	14.09	15.48	17.00	18.40
Na_2O	43.00	37.00	31.00	28.91	27.52	26.00	24.60
Al/Na	0	.16	.39	.49	.56	.65	.75

	X-1881	X-1882	X-1883	X-1962	X-1884
SiO_2	57.00	57.00	57.00	57.00	57.00
Al_2O_3	21.50	24.50	27.50	29.00	30.50
Na_2O	21.50	18.50	15.50	14.00	12.50
Al/Na	1.00	1.33	1.78	2.07	2.44

TABLE II - (Continued)

Series VII

	X-1938	X-1939	X-1940	X-1941	X-1942	X-1943	X-1944
SiO_2	50.00	50.00	50.00	50.00	50.00	50.00	50.00
Al_2O_3	-	6.00	12.00	18.00	21.50	25.00	29.00
Na_2O	50.00	44.00	38.00	32.00	28.50	25.00	21.00
Al/Na	0	.14	.32	.56	.76	1.00	1.38

Series VII - (Continued)

	X-1958	X-1945
SiO_2	50.00	50.00
Al_2O_3	31.00	33.00
Na_2O	19.00	17.00
Al/Na	1.63	1.94

charge the bushing. Fibers between 0.00035 and 0.00040 inch in diameter were formed for tensile strength measurements. Virgin fibers were collected on forks, placed in a desiccator, and tested promptly in the manner previously described. At least three sets of fibers sufficient to give fifteen breaks each were tested for each glass. Results reported are usually the average of the results for the two closest sets. In a few cases, additional sets of fibers were tested, in which case the averages reported are for more than two sets.

Modulus of elasticity measurements were made on fibers in the 0.00075 to 0.00085 inch diameter range by measuring the elongation under load. This size of fiber was selected because it was convenient to form and to measure. Some difficulty was found in obtaining reproducible results with fibers varying widely in fiber diameter. Although the source of difficulty was never completely isolated, it was found that reproducibility was reasonably good when measurements were performed on fibers of this selected diameter range only. Each point reported is the average of at least eight measurements on four fibers.

(3) A rough measurement of relative viscosities of the glasses was made by noting the bushing temperature at which fibers were formed. Results are approximate only, since no effort was made to calibrate thermocouples, or to compensate for any drift in thermocouple output that may have occurred as they aged. Also, several different bushings were used, with possible bushing-to-bushing variation.

TABLE III

COMPOSITIONS IN MOL PER CENT
SiO_2-TiO_2-K_2O SYSTEM

	X-1926	X-1927	X-1928	X-1929	X-1930	X-1931	X-1932
SiO_2	60.0	60.0	60.0	60.0	60.0	60.0	60.0
TiO_2	-	5.0	10.0	15.0	20.0	25.0	30.0
K_2O	40.0	35.0	30.0	25.0	20.0	15.0	10.0

	X-1946	X-1947	X-1948	X-1949	X-1950	X-1951
SiO_2	70.0	70.0	70.0	70.0	70.0	70.0
TiO_2	-	5.0	10.0	15.0	20.0	25.0
K_2O	30.0	25.0	20.0	15.0	10.0	5.0

	X-1977	X-1976	X-1979	X-1980
SiO_2	80.0	80.0	80.0	80.0
TiO_2	-	5.0	10.0	15.0
K_2O	20.0	15.0	10.0	5.0

	X-1981	X-1982	X-1983	X-1984	X-1985	X-1986	X-1987
SiO_2	50.0	50.0	50.0	50.0	50.0	50.0	50.0
TiO_2	40.0	35.0	30.0	25.0	20.0	15.0	10.0
K_2O	10.0	15.0	20.0	25.0	30.0	35.0	40.0

	X-1992	X-1993	X-1994	X-1995	X-1996	X-1997	X-1998
SiO_2	40.0	40.0	40.0	40.0	40.0	40.0	40.0
TiO_2	10.0	15.0	20.0	25.0	30.0	35.0	40.0
K_2O	50.0	45.0	40.0	35.0	30.0	25.0	20.0

	X-1999	X-2000
SiO_2	40.0	40.0
TiO_2	45.0	50.0
K_2O	15.0	10.0

b. SiO_2-TiO_2-K_2O System

(1) Compositions Studied

Table III gives the compositions studied in mol percentages.

(2) Preparation and Testing of Specimens

Glasses were prepared, fiberized, and tested as described for the glasses in the silica-alumina-soda system.

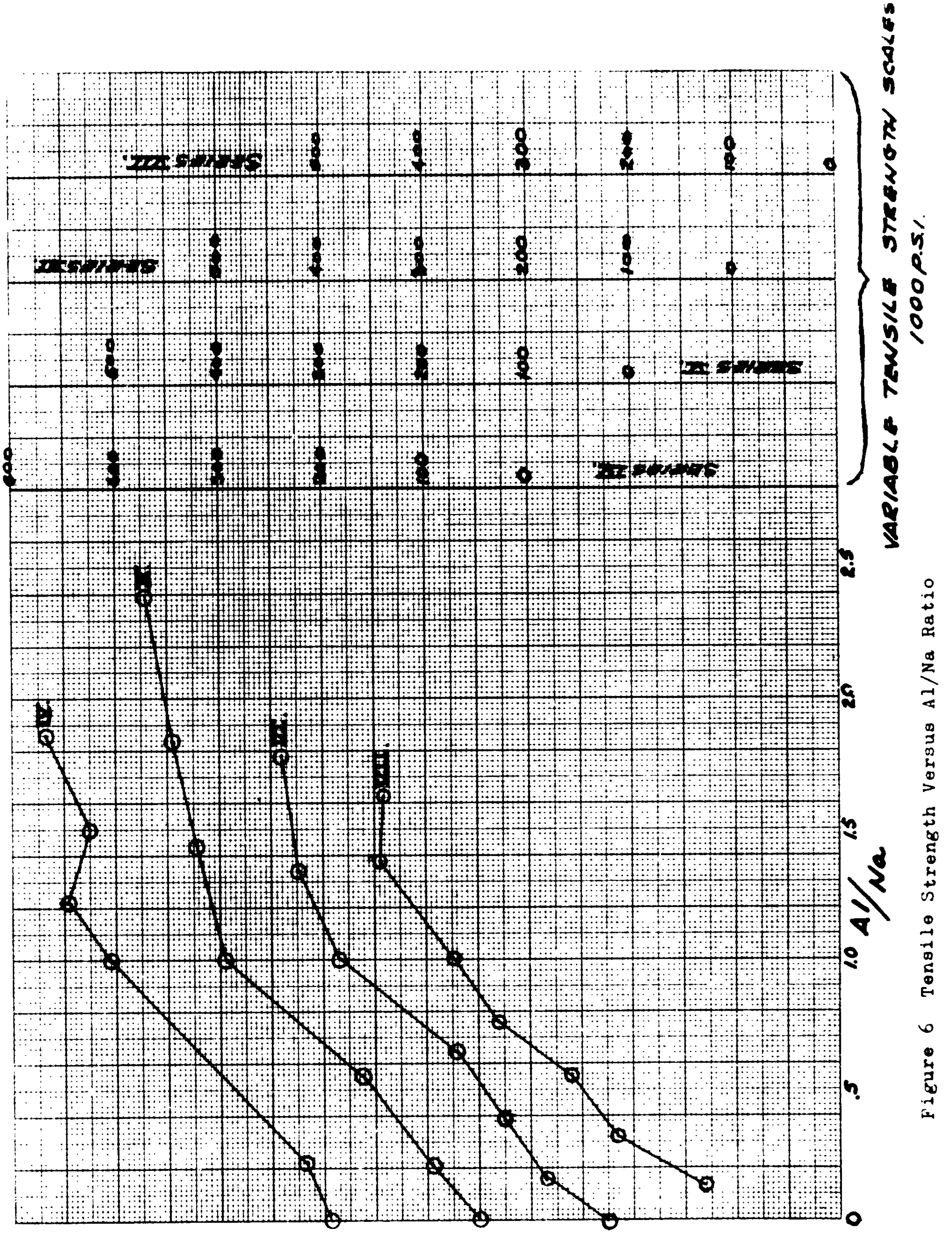


Figure 6 Tensile Strength Versus Al/Na Ratio

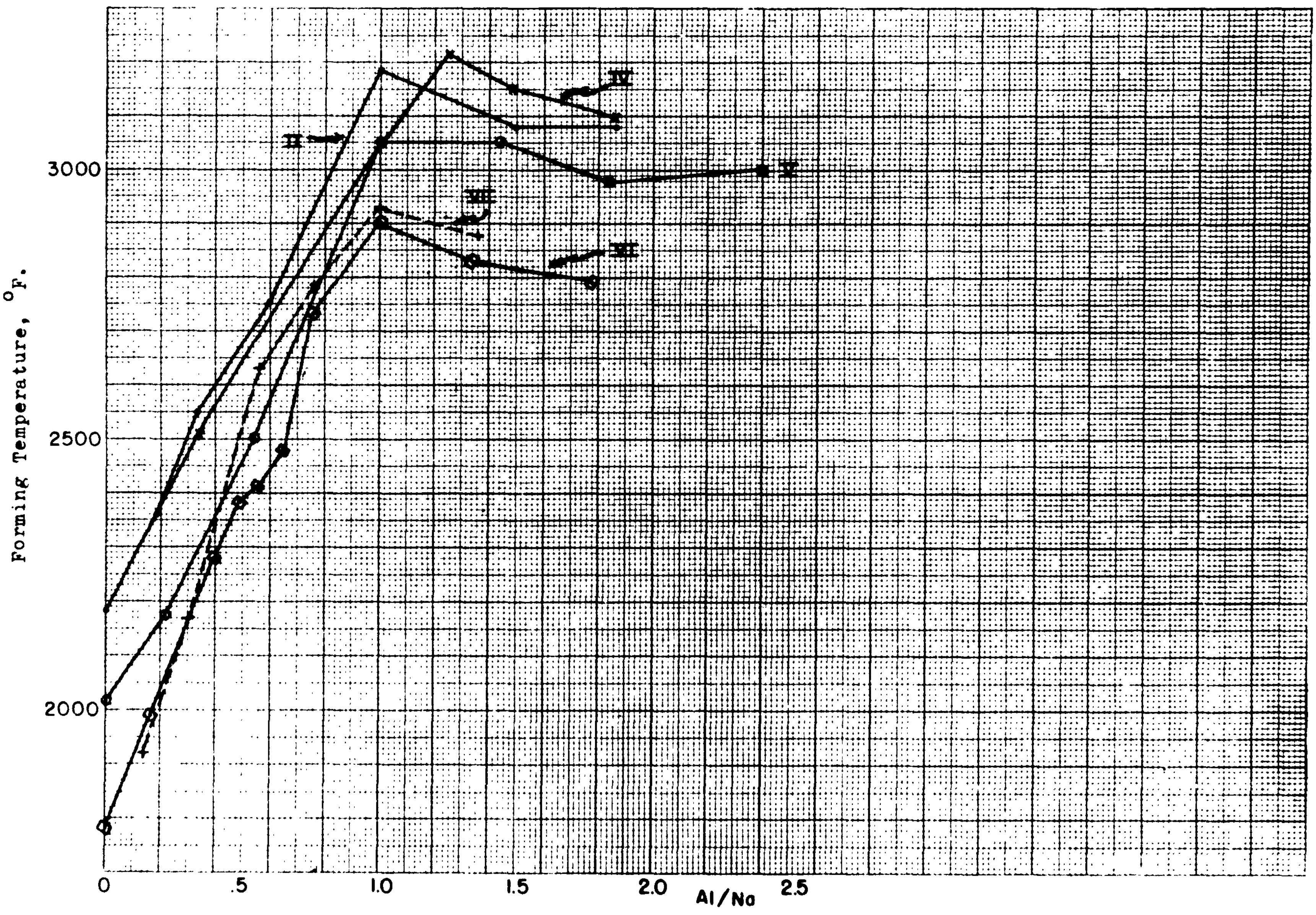


Figure 7 Forming Temperature Versus Al/Na Ratio

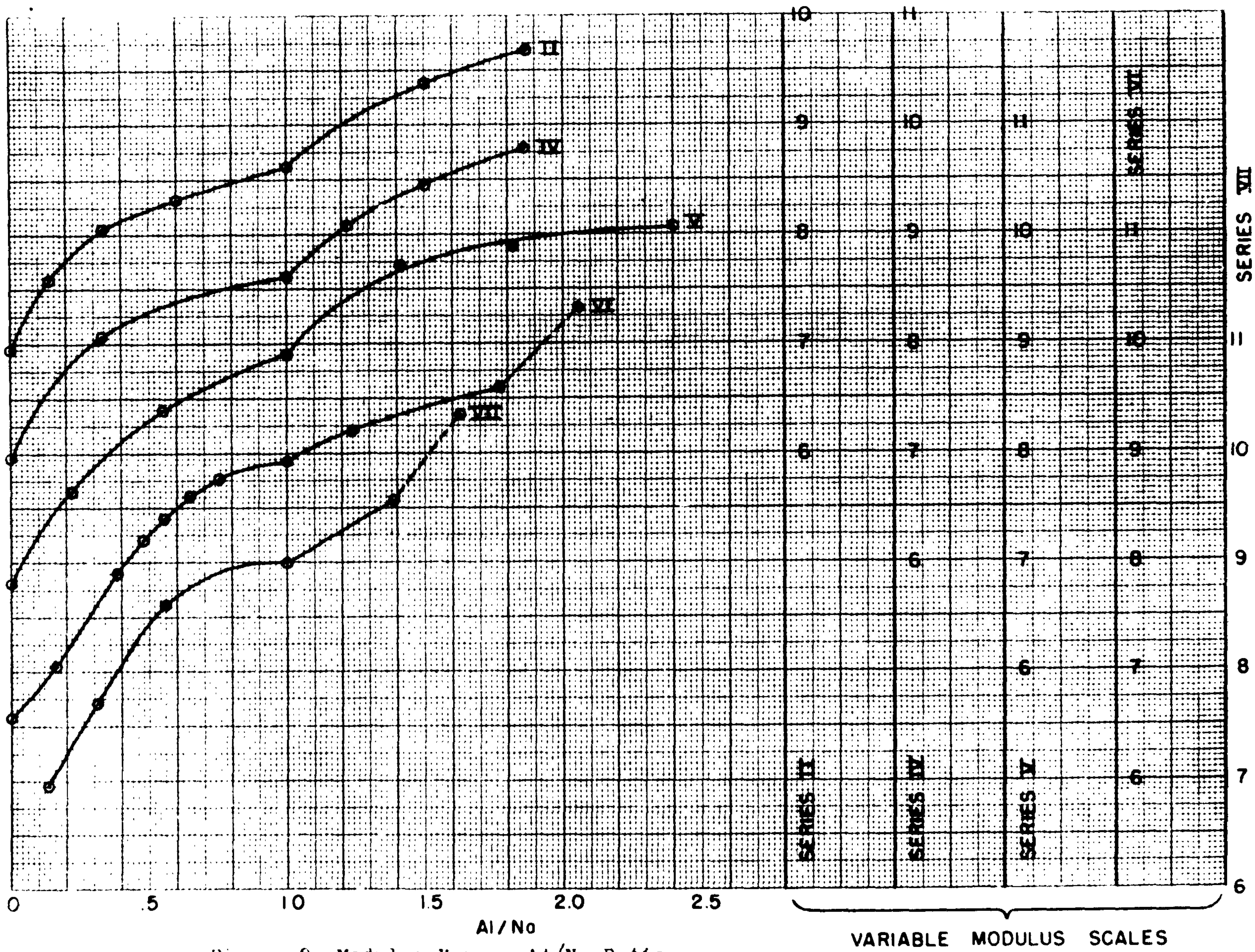


Figure 8 Modulus Versus Al/Na Ratio

3. Experimental Results

a. SiO_2-Al_2O_3-Na_2O System

(1) Tensile Strength

Tensile strength results are summarized in graph form in Figure 6. A separate scale was used for each series of glasses, as indicated on the right of the graph, so that all data could be presented on one sheet without having curves overlap. Tensile strength increases in all cases as the Al to Na ratio increases. It appears that there is an inflection in all curves at or near an Al to Na ratio of one, such that the rate of increase of strength is less at the higher ratios.

(2) Viscosity Measurements

In Figure 7 are given the data for viscosity (fiber forming temperature) vs. the Al to Na ratios of the glasses.

Viscosity increases rapidly with increasing Al to Na ratio up to a ratio of one. Above this, the viscosity levels off or decreases slightly.

(3) Modulus of Elasticity

The data on modulus measurements are plotted in Figure 8. Again a separate scale is used for each series of glasses, so that all curves may be plotted on the same sheet without overlapping. There is an inflection point for all curves at an Al to Na ratio of one. All curves have approximately the same shape. Curves for Series VI and VII may be exceptions,since the locations of the last points indicate that they may rise quite steeply at the higher Al to Na ratios. However, the glasses for which these points were obtained were fiberized with difficulty because of devitrification. These points are therefore questionable. The last parts of the curves are dotted to indicate this.

The data were plotted in various ways to find whether some other significant relationship might be found. Figure 9 shows modulus plotted vs. the ratio of (Si + Al) to O. These curves show an inflection where the ratio is 0.50. This corresponds to the compositions for which the Al to Na ratio is one. However, the curves in Figure 9 show another inflection, where the ratio of (Si + Al) to O is 0.46 or 0.47. Several additional melts were made in Series VI to establish more accurately the location of the inflection and to determine how sharp the break might be. For this series, the inflection appears to be at 0.475 and to follow a smooth curve rather than to have a sharp break. The data are not complete enough or precise enough to show the exact location and nature of the inflections in the other curves. However, all seem to have some kind of a break in about the same region. When plotted in the same way, tensile

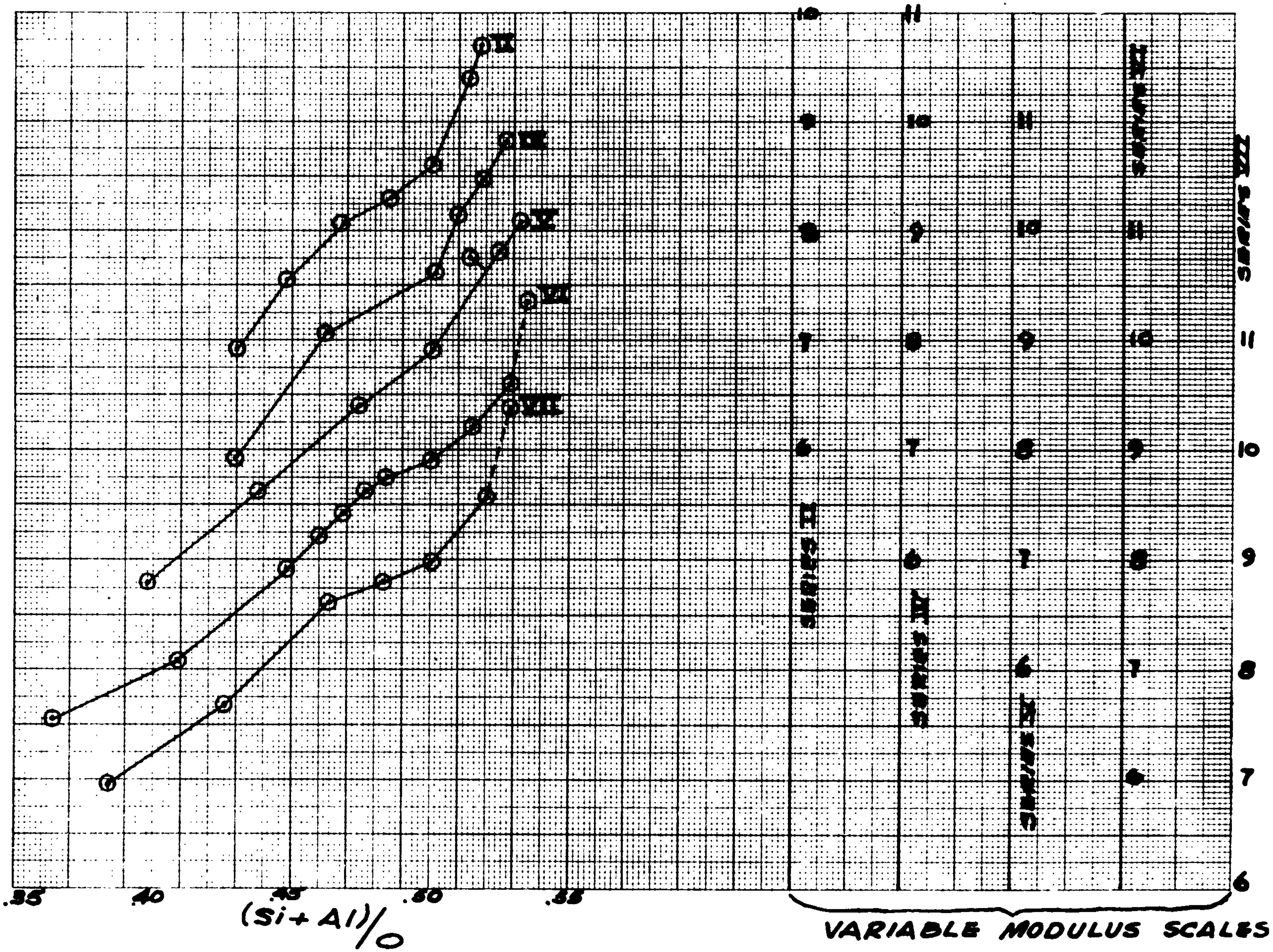


Figure 9 Modulus Versus (Si + Al)/O Ratio

TABLE IV

MODULUS OF AS DRAWN AND ANNEALED FIBERS

SiO_2-Al_2O_3-Na_2O SYSTEM

PSI x 10^6

GLASS NO.	AS DRAWN	ANNEALED
X-1580A	6.91	8.05
X-1591B	8.06	8.98
X-1592B	8.60	9.60
X-1593A	9.13	10.01
X-1594A	9.44	10.32
X-1595A	9.78	11.01
X-1866	6.79	7.71
X-1867	7.60	8.80
X-1868	8.38	9.51
X-1869	8.87	9.78
X-1870	9.75	10.41
X-1871	9.82	10.60
X-1877	6.53	7.63
X-1878	7.05	8.25
X-1879	7.92	8.99

strength and viscosity curves may also show similar behavior, but results are less well defined. The significance of the breaks in this region has not yet been established.

A number of modulus measurements were made on annealed fibers. Work on annealed fibers was dropped when it became apparent that the information obtained did not justify the additional effort. In general, annealed fibers had moduli about 1,000,000 psi higher than those of fibers as drawn. Table IV lists moduli obtained on fibers as drawn and annealed for those glasses for which data are available.

Modulus data were plotted in a manner such that interpolated values could be obtained for constructing a diagram showing lines of constant modulus vs. composition. Results are shown in Figure 10. The dotted lines are lines of constant modulus of the indicated values. The five series of glasses studied fall on the dashed lines labelled with the appropriate Roman numerals. (Only the top portion of the three-component system from SiO_2 = 50% upwards is shown.) The phase boundaries and primary phases for this system reported in the literature(4) are also shown. This was done to show whether transitions from regions characteristic of one phase to another would be accompanied by breaks in the constant modulus curves. The data do not show any clear indication of such behavior. The change of modulus from 8.0 to 9.0 x 10^6 psi requires a larger change in composition than a change of

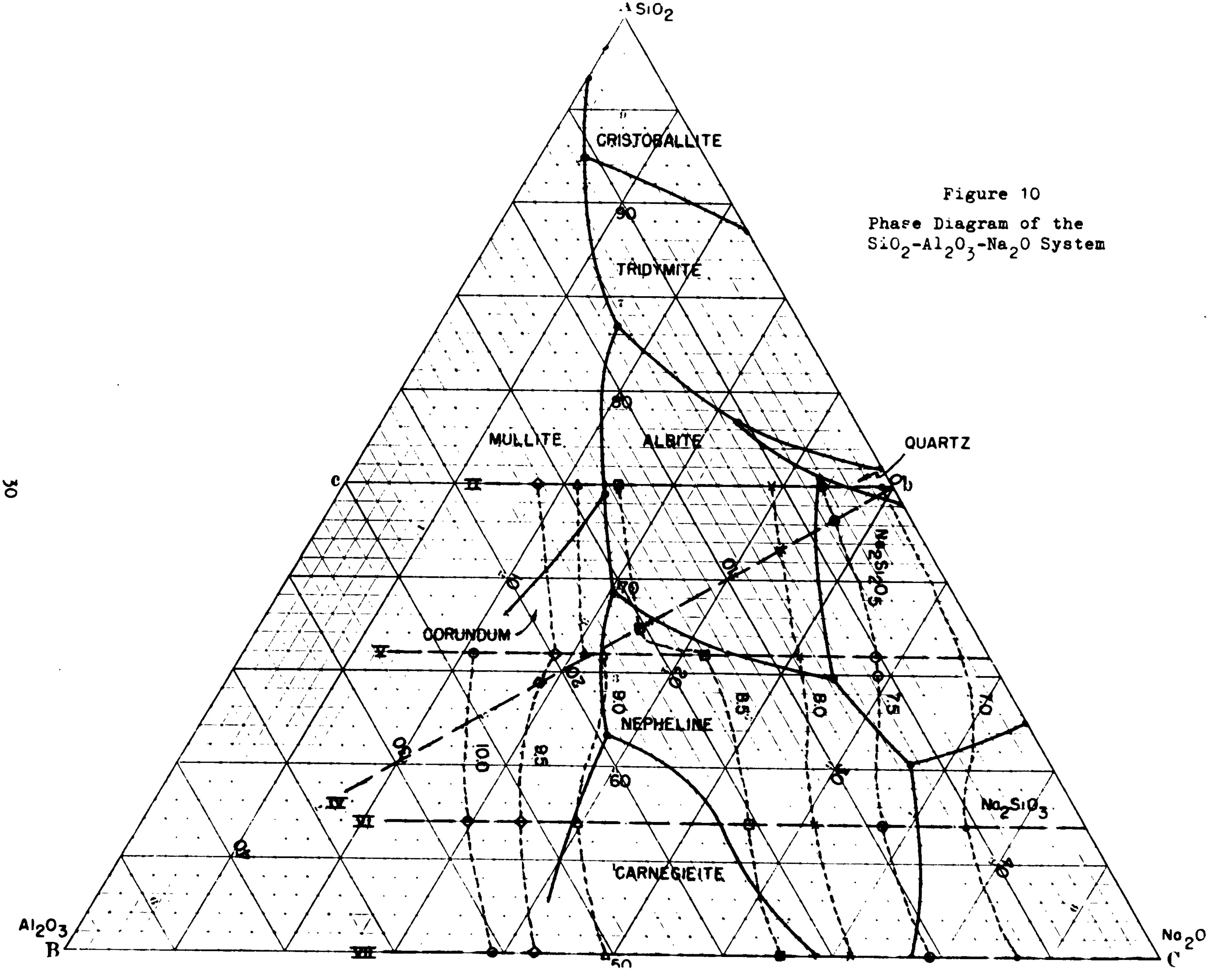


Figure 10

Phase Diagram of the SiO_2-Al_2O_3-Na_2O System similar magnitude at either higher or lower values of modulus. The constant modulus curve for modulus of 8.5×10^6 psi shows two breaks, whereas all other lines are nearly straight with only slight curvatures. The region in which this break occurs corresponds to the compositions for which the (Si + Al) to O ratio is 0.46 to 0.47.

This is the range of values in which a second break in the modulus curves was shown in Figure 9.

b. SiO_2-TiO_2-K_2O System

(1) Tensile Strength

Tensile strength results are summarized in graph form in Figure 11. Results are plotted vs. the TiO_2 to K_2O ratio. Any change in properties resulting from a change in the coordination number of the titanium might be expected to be a function of this ratio, since it is related to the amount of oxygen available in the system for coordinating with the titanium.

At the 60% SiO_2 level, it appears that there is a break in the curve at a ratio of one. At the 70% level, the curve is smooth, but it does have an inflection in this region. At the lower SiO_2 levels, it is not possible to be certain whether or not there is any meaningful break in the curves. The precision of the measurements is lower at the very low strengths involved. In addition, the glasses with the lower ratios have such poor durability that chemical attack on the fibers by the moisture of the air during the testing time could contribute to inaccuracies.

Examination of the published data on other physical properties of glasses in this system suggested that the position at which properties changed was dependent also upon the SiO_2 content. For this reason, the curves shown in Figure 12 were prepared showing the tensile strength as a function of the ratio of SiO_2 + TiO_2 to K_2O. The curves for 70 and 60% SiO_2 glasses are approximately parallel, but the other two do not appear to fit this pattern.

(2) Viscosity Measurements

The fiber forming temperatures are plotted as a function of TiO_2 to K_2O ratio in Figure 13. There is a suggestion of a break in the curve for the 60% SiO_2 series at a ratio of somewhat less than one. The rest of the curves approach a straight line relationship very closely.

Two curves are given for the 60% SiO_2 series. The one drawn as a solid line was obtained when the fibers tested for strength and modulus were run. When it became apparent that these results were inconsistent, the glasses were re-run to

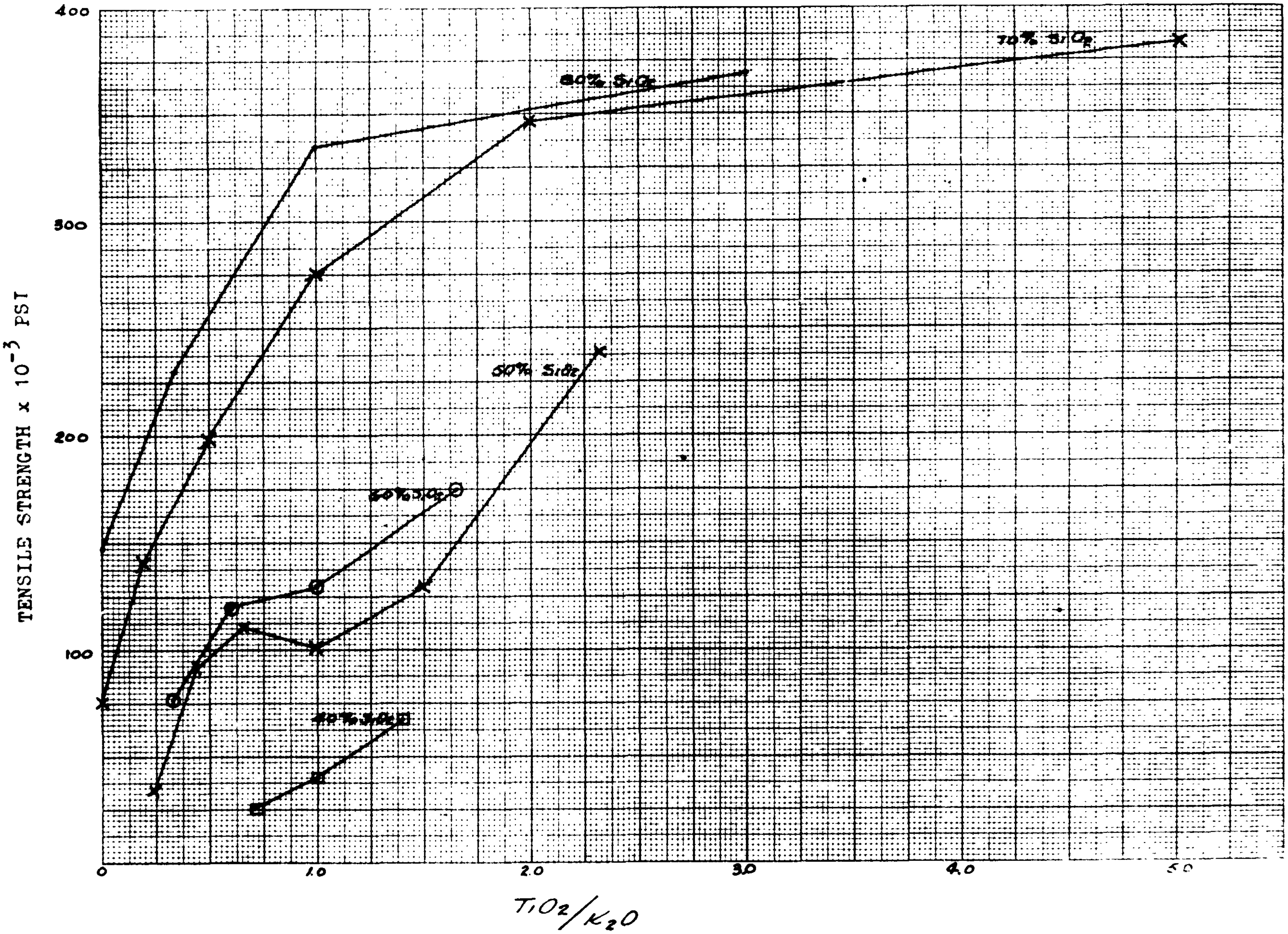


Figure 11 Tensile Strength Versus TiO_2/K_2O Ratio

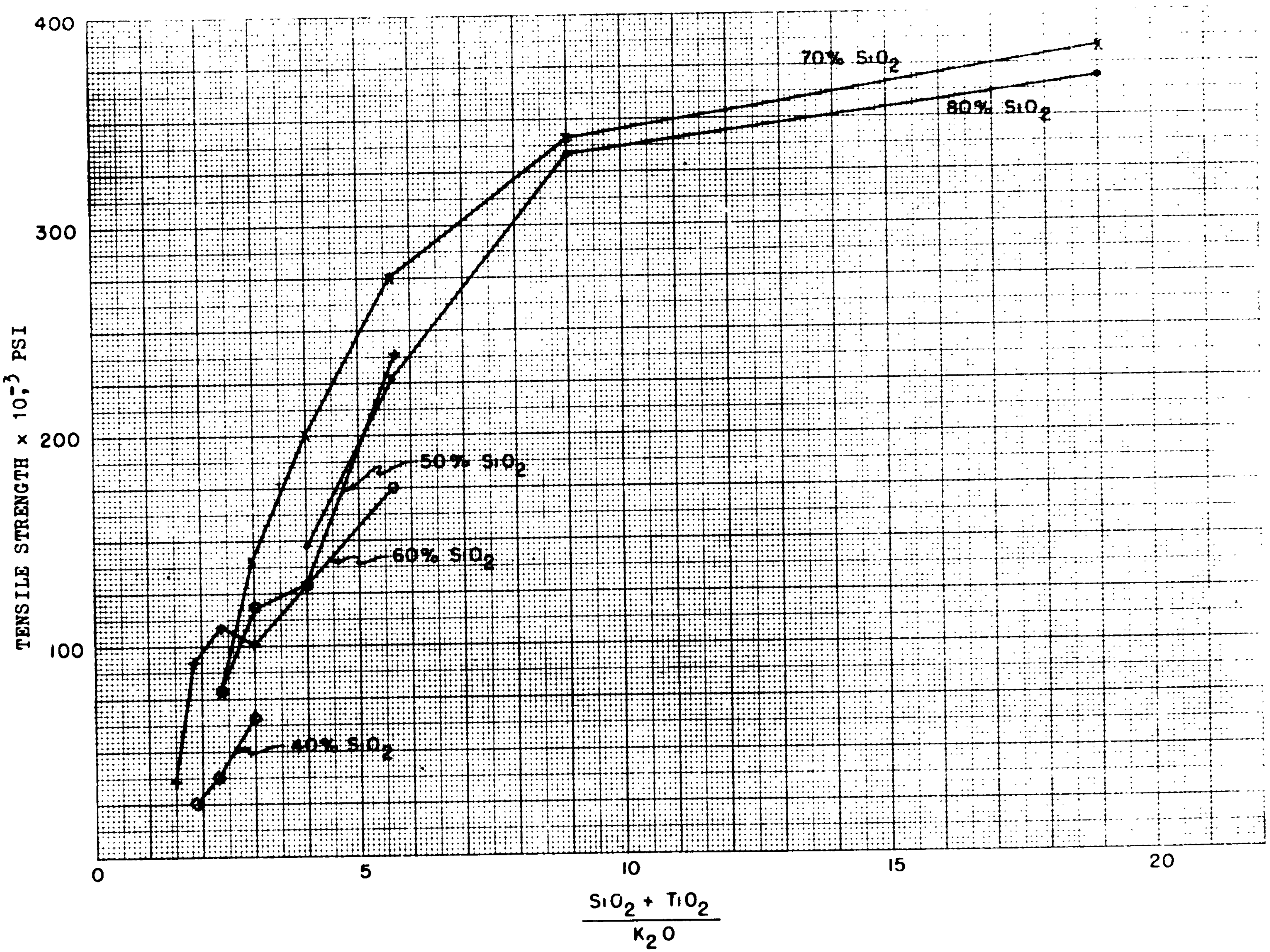


Figure 12 Tensile Strength Versus (SiO_2 + TiO_2)/K_2O Ratio

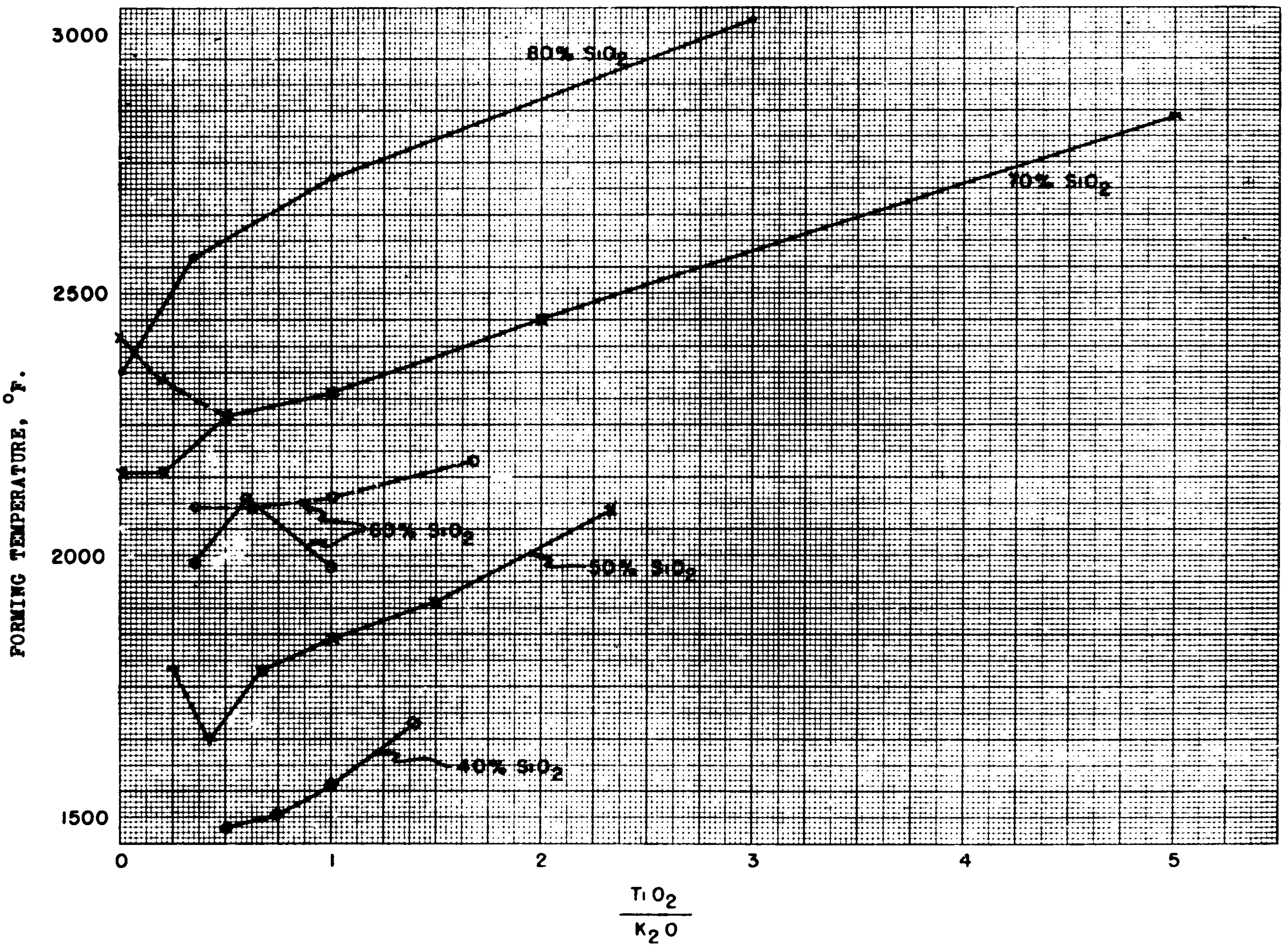


Figure 13 Forming Temperature Versus TiO_2/K_2O

determine fiber forming temperatures only. The results are shown on the curve drawn in a dotted line. The re-run indicated that these glasses must have a very flat viscosity curve, that is, a relatively large change in temperature is required to produce a given change in fiber diameter. This could account in part for the unusual shape of the original curve. Care was taken to obtain forming temperatures at very nearly the same fiber diameters on the second run. Therefore, this curve is to be regarded as more reliable. The second curve was obtained with a different bushing. Small differences in bushing construction or thermocouple output may have caused the position of the curve to be generally higher than that obtained on the first run. The slope of the curve seems to be less at the 60% SiO_2 level than at either higher or lower levels.

The point at the lowest TiO_2 to K_2O ratio for the 50% SiO_2 series was obtained the day the thermocouple on the bushing failed. Its accuracy is therefore suspect.

Forming temperature data were re-plotted in Figure 14, showing forming temperature vs. the SiO_2 + TiO_2 to K_2O ratio. The curves have about the same shape and relationship to each other as shown on Figure 13.

(3) Modulus of Elasticity

Modulus results are plotted as a function of the TiO_2 to K_2O ratio in Figure 15. The curves are all similar in shape. The curve at the 70% SiO_2 level appears to be out of place at the upper end in that it crosses those for the 50% and 60% SiO_2 levels. The other curves seem to approach the same value at a TiO_2 to K_2O ratio of 3.0.

None of the curves show a sharp break, although all curve downward in the general vicinity where the TiO_2 to K_2O ratio is one.

When modulus is plotted vs. the SiO_2 + TiO_2 to K_2O ratio, Figure 16, all curves seem to fall into a consistent pattern. One point on the curve for the 50% SiO_2 level appears to be off, but it did not fit the apparent curve in Figure 15 either.

4. Discussion of Results

In the SiO_2-Al_2O_3-Na_2O system, the three properties measured- fiber forming temperature, tensile strength, and modulus of elasticity - appear to be dependent upon glass structure in the same manner as other physical properties reported in the literature. A break in composition vs. property curves was found where the Al to Na ratio for the glass was one. The suggestion that this is related to a change in coordination number of the alumina is consistent with these observations. Glass viscosity (as shown by fiber forming temperature)

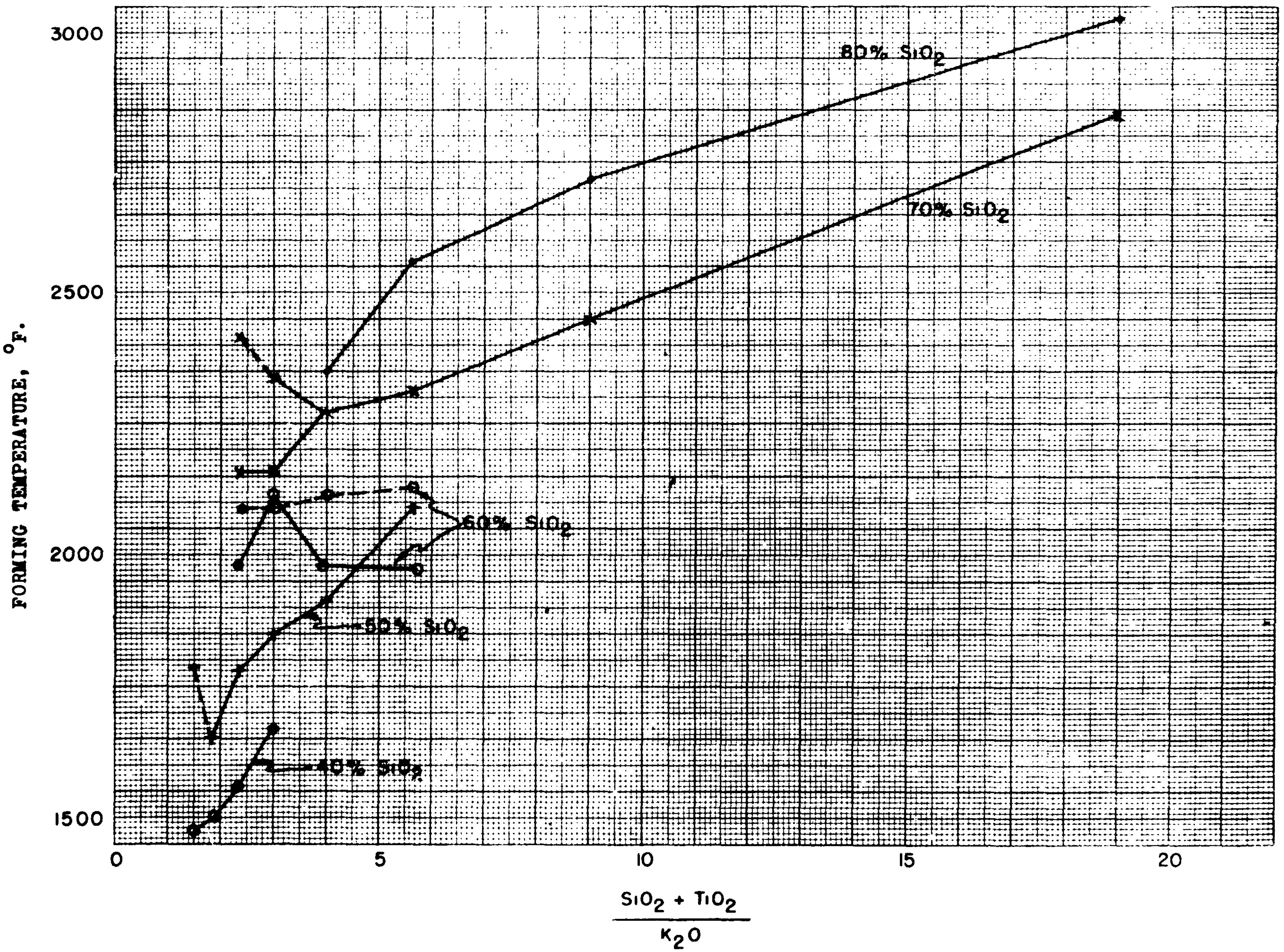


Figure 14 Forming Temperature Versus $(SiO_2+TiO_2)/K_2O$ Ratio

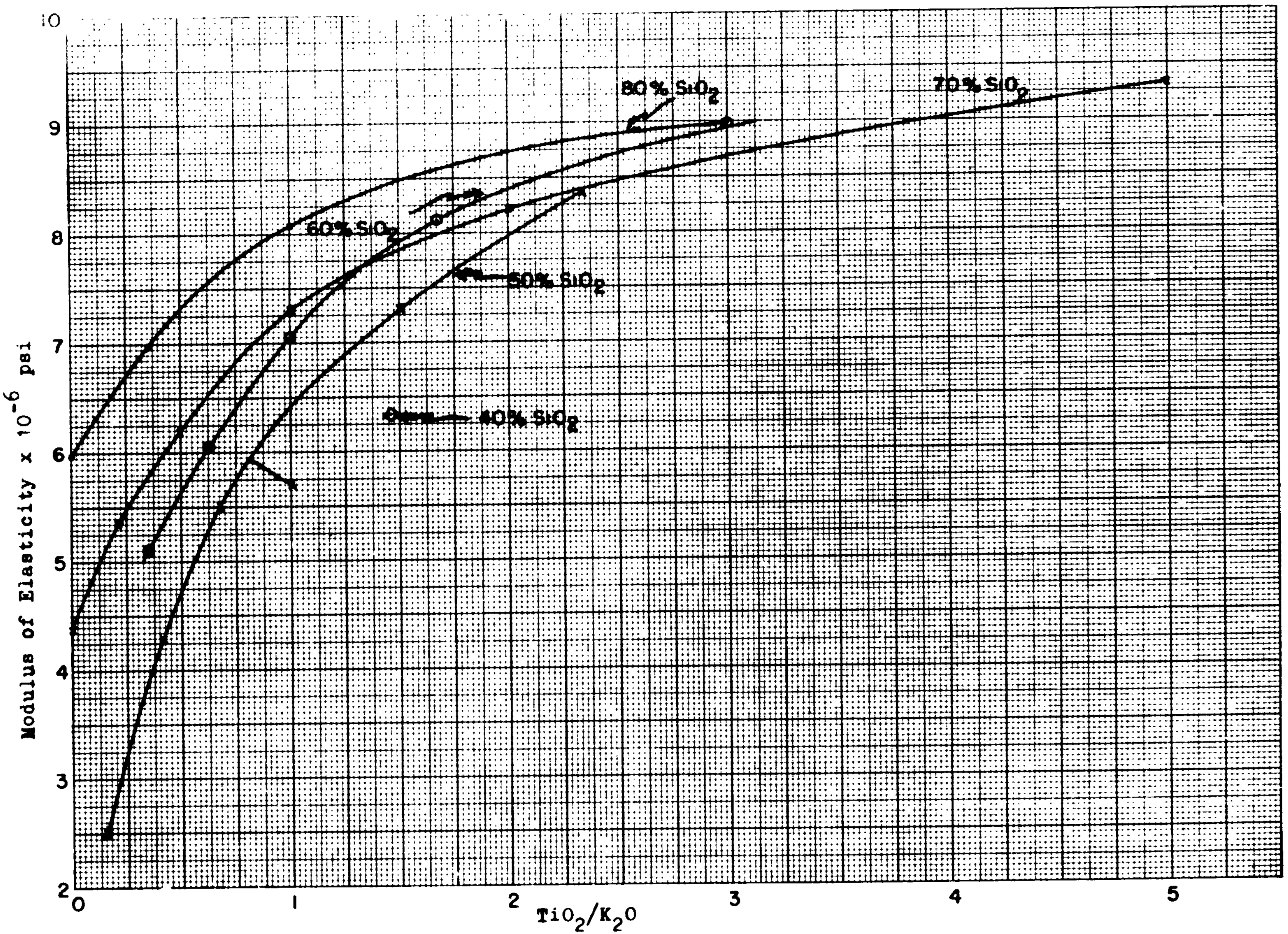


Figure 15 Modulus Versus TiO_2/K_2O Ratio

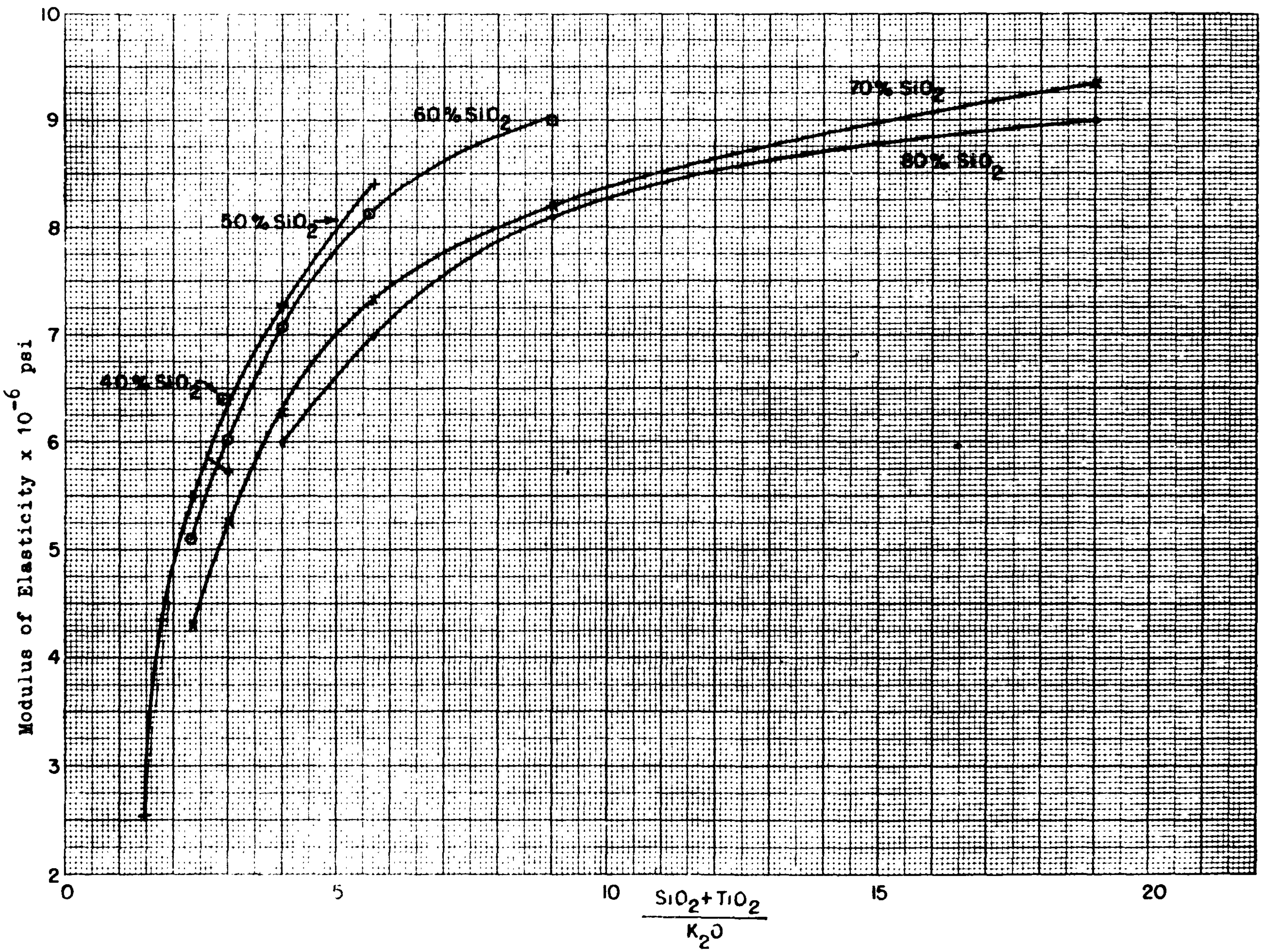


Figure 16 Modulus Versus $(SiO_2+TiO_2)/K_2O$

increases at first as Al_2O_3 is substituted for Na_2O. This is logical if the Al_2O_3 enters the network and behaves much as SiO_2 would. At higher Al_2O_3 contents where the Al to Na ratio exceeds one, the aluminum added enters the structure with a coordination number of six, and acts as most glass modifiers do, by lowering the viscosity. Similarly, substitution of Al_2O_3 for Na_2O increases the tensile strength, by increasing the proportion of ions participating in the network. Strength continues to increase, but at a lower rate, at ratios of Al to Na higher than one. It could be expected that viscosity might be related to tensile strength in that both are dependent upon the forces holding the network together, and that if a change in composition caused the viscosity to drop, the tensile strength should drop also. Two possible reasons for the results actually obtained are suggested:

a. Forming temperature may not be a simple function of viscosity. Surface tension, for instance, can affect forming behavior, and might change in such a way as to counteract changes in viscosity.

b. The cooling of the glass may be accompanied by further structural changes which make it behave differently at room temperature than it would at elevated temperatures.

Measurements of the modulus of elasticity show the break at the Al to Na ratio of one more clearly and consistently than to tensile strength or forming temperature. This is not surprising. Tensile strength of fibers is known to be closely related to the conditions under which they were formed. Attempts were made to keep forming conditions similar for the fibers tested in this study. However, it is quite possible that if enough conditions had been tried to find the optimum strength for each composition,some inconsistencies in the data would have disappeared. The measurement of forming temperature was just incidental, and was not the primary purpose of the work. Hence, precautions that could have been taken to increase accuracy were not observed, and results are expected to contain small errors. Modulus results, on the other hand, seem to be less sensitive to variations in forming conditions. The precision is believed to be relatively good, at least when the diameters of the fibers tested lie in a small range. The spread in results for the eight or more determinations made for each point reported was usually not more than 0.3×10^6 psi, and normally less than this.

The nature of the change in modulus as the Al to Na ratio increases is somewhat surprising. A structural change which results both in lowered viscosity and a reduction in slope of the tensile strength curve causes an increase in the modulus. It may be that the larger size structural units resulting from six-coordinated aluminum can increase the rigidity of the structure without increasing its strength.

Recently Lacy(5) offered another proposal for the structure of glasses in the SiO_2-Al_2O_3-Na_2O system. He suggested that the logical packing of ions favors the formation of what he calls "triclusters." These triclusters consist of three tetrahedral groups having a common oxygen, which is shared by an AlO_4 group and two SiO_4 groups or an SiO_4 and two AlO_4 groups. Each two triclusters conserve one oxygen. When the Al to Na ratio is greater than one, there are not enough oxygens for all glass formers to be in tetrahedral groups. According to Lacy, the formation of triclusters compensates for this oxygen shortage. This theory would probably account for the observed results as well as the concept of change in coordination numbers if we assign suitable properties to the triclusters. The data do not seem to support one concept over the other.

The properties measured on the glasses in the SiO_2-Ti_2O -K_2O system do not appear to lead to as good a concept of glass structure. Examination of Figures 15 and 16 shows that the modulus increases as either the TiO_2 to K_2O or the SiO_2 + TiO_2 to K_2O ratio increases. The rate of increase drops off at the higher ratios. The absence of any sharp break in the curves suggests that the change in slope does not result from a sudden change in structure at some particular composition. If, for instance, a change in coordination number of the titanium is responsible, it seems likely that titanium is present to some degree in both states in all glasses studied. Changes in composition thus probably change the relative amounts in some rather gradual fashion. That the change in structure is affected also by the SiO_2 content is suggested by the fact that the data seem to fall into a systematic system of curves in Figure 16, while there is some crossing of curves in Figure 15, in which no account is made of the SiO_2 content.

It might be argued that Figures 11 and 12 do not support the latter contention in that curves for tensile strength seem to show a more orderly relationship when plotted vs. the TiO_2 to K_2O ratio than when plotted vs. the SiO_2 + TiO_2 to K_2O ratio. However, examination of Figure 12 suggests that it is possible that the proper order of the curves for the various series of glasses might be the same as that found for modulus. At the very low ratios of SiO_2 + TiO_2 to K_2O, the curves tend to fall in the same order as the modulus curves in Figure 16. The peculiar shapes of the tensile strength curves at the 50% and 60% SiO_2 levels do not seem logical and may indicate experimental error.

Figure 17 was plotted to assist in plotting lines of constant modulus on a three-component diagram. It appears that at any SiO_2 level the modulus may be a linear function of the K_2O content of the glass.

The constant modulus curves are plotted in Figure 18. These curves appear to offer no particularly significant implications relative to glass structure.

The SiO_2-Al_2O_3-K_2O system should be studied as the SiO_2-Al_2O_3-Na_2O and the SiO_2-TiO_2-K_2O systems have been. Results should be studied to determine if some correlation between the two systems can be found.

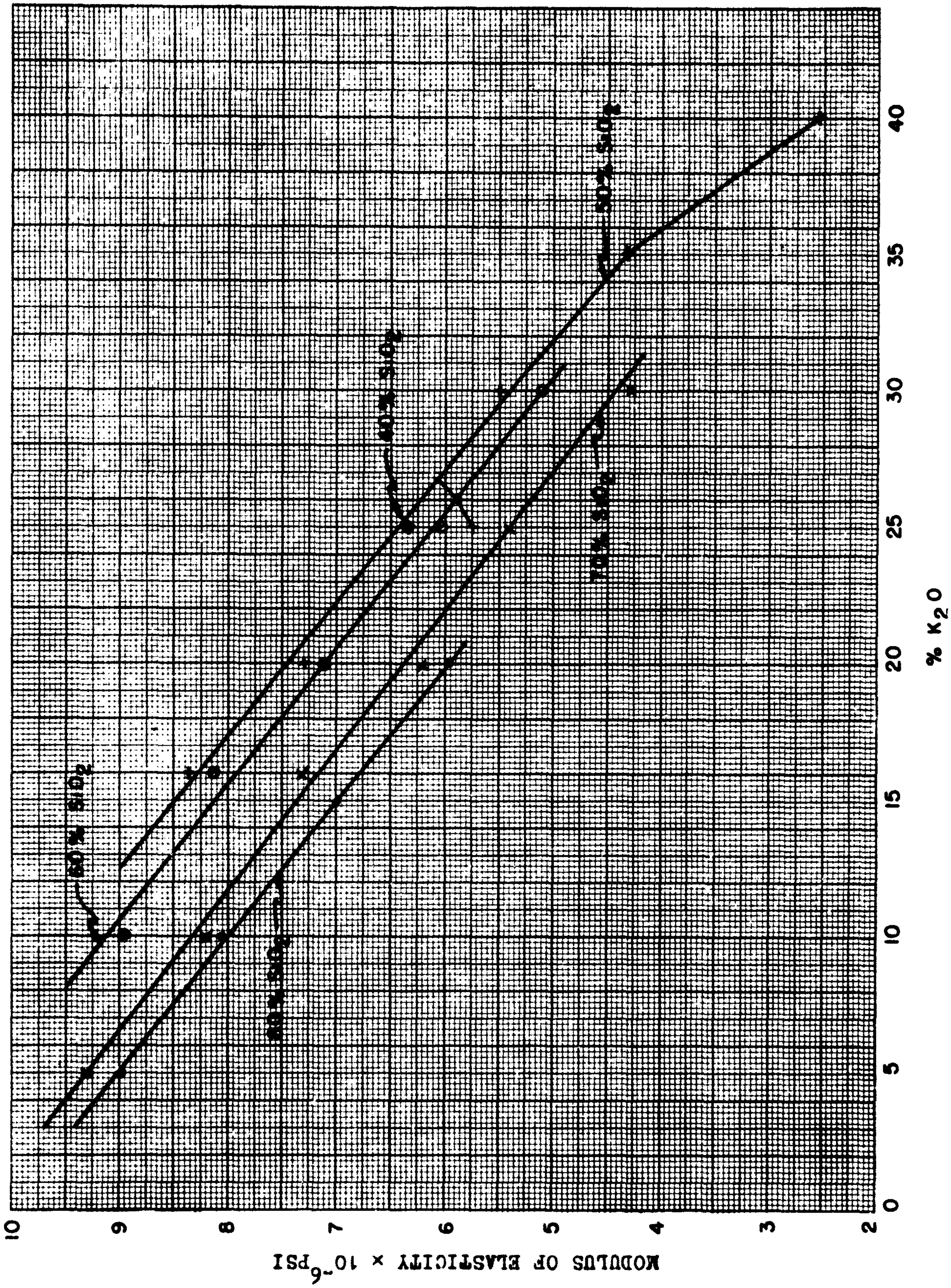


Figure 17 Modulus Versus Percent K$_2$O

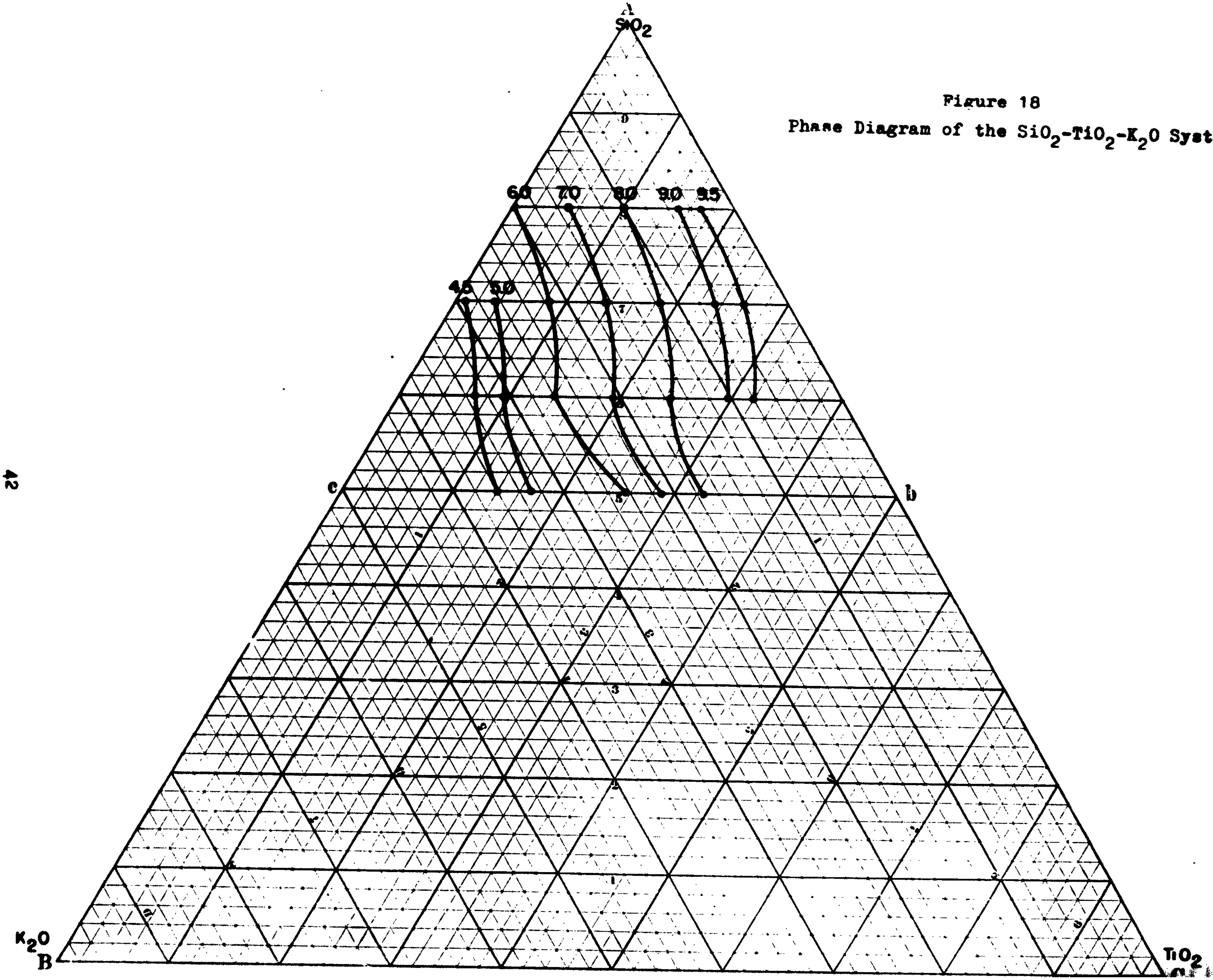


Figure 18

Phase Diagram of the SiO_2-TiO_2-K_2O Syste

Differences between the SiO_2-Al_2O_3-K_2O system and the SiO_2-Al_2O_3-Na_2O system should be examined to see if they can be related to the size of the alkali ion added. If such relation is found, study of a system utilizing a third alkali ion, probably lithium, should be undertaken.

III

CONCLUSIONS

The results of this investigation indicate that glass fibers possessing the highest tensile strength and modulus of elasticity values are located in the SiO_2-Al_2O_3-MgO and the SiO_2-Al_2O_3-ZnO systems. There is some indication that the SiO_2-Al_2O_3-BeO system may also possess desirable properties.

The best glass compositions in the SiO_2-Al_2O_3-MgO system fall at an Al_2O_3 to MgO mol ratio of approximately 1.0 and contain from 60 to 70% by weight of SiO_2. The SiO_2-Al_2O_3-ZnO system has not been investigated extensively, but it is expected that the glasses with the best properties are located within a similar range of values. Investigation of the SiO_2-Al_2O_3-BeO system should be continued, but is complicated by the extreme devitrification tendencies of this glass.

The addition of a fourth oxide component to a base glass consisting of the S-994 composition does not improve the tensile strength or modulus of elasticity of the resultant glass. The addition of minute quantities of a fourth oxide component has received only preliminary study, but might prove beneficial.

The exact effect of fiber diameter on both tensile strength and modulus is still open to question. However, there is some evidence that a reduction in diameter of SiO_2-Al_2O_3-MgO and SiO_2-Al_2O_3-ZnO glass fibers does improve properties, especially the modulus of elasticity.

IV

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13. ABSTRACT The results of the present investigation have shown that glass fibers drawn from compositions located in the SiO_2-Al_2O_3-ZnO system possess tensile strengths in excess of 800,000 psi. Glass fibers drawn from compositions in the SiO_2-Al_2O_3-MgO system have given similar results, particularly at fiber diameters in the 0.00015 to 0.00020 inch range. The modulus of elasticity of glass fibers obtained from compositions located in the SiO_2-Al_2O_3-MgO system can be increased to 16.0×10^6 psi. This is accomplished by lowering the fiber diameter to the 0.00015 to 0.00020 inch range.

In the SiO_2-Al_2O_3-Na_2O system, the fiber forming temperature, the tensile strength and the modulus of elasticity change with composition in a manner which gives a break in the composition vs. property curves at the point where the Al to Na ratio is 1. This is related to the change in the coordination number of the aluminum at this ratio which has been proposed in the literature.

The properties measured for glasses in the SiO_2-TiO_2-K_2O system do not appear to lead to as clear a concept of glass structure. Properties very gradually with composition, with no evidence of a sharp break at any point. There is some indication that the rate of change of properties is dominated more by the silica content than is the case in the SiO_2-Al_2O_3-Na_2O system.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fibers, glass, composition, strength, modulus						

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