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Tellurite Glasses

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The boundaries of regions of glass-forming compositions were determined in binary tellurite systems with alkali, alkaline-earth, and heavy-metal oxides, and in the ternary systems TeO_2–WO_3–Ta_2O_5, TeO_2–WO_3–BaO, TeO_2–WO_3–Bi_2O_3, and TeO_2–WO_3–Tl_2O. On the basis of a structural interpretation of liquid immiscibility in binary oxide systems and of X-ray diffraction investigation of the structure of tellurite glasses, a crystallochemical interpretation of glass formation is proposed, as well as a method for calculating the modifier-poor boundaries of the regions of glass-forming compositions in binary systems. An investigation of the crystallizability, density, optical constants, spectral transmission characteristics, and chemical durability of the tellurite glasses as functions of their chemical compositions has led to the development of a new flint-type optical glass, with $n_d = 2.1608$ and $\nu = 17.4$, possessing a high chemical durability and resistance to devitrification.

I. Introduction

HIGH-INDEX glasses in combination with low-index glasses of the same dispersivity may reduce the spherical aberration in optical systems and may be used for dispersion prisms in spectroscopic instruments as well as for negative elements in short-focus achromatic lenses.

The highest refractive indices of commercially available optical glasses are about 1.9 to 2.0. Published data on glasses list refractive indices ranging from 2.0 to 2.1 but such glasses crystallize readily, have poor homogeneity, and are chemically unstable. There is no published information on optical glasses with refractive indices above 2.0 which might be suitable for industrial use.

The principal purpose of this study was to develop optical glasses with refractive indices above 2.1 and to investigate some of their properties as a function of composition. Glasses in which tellurium dioxide is the glass-forming component[1(a)] are the most suitable for this purpose.

In developing new optical glasses for commercial production it is necessary to discover what chemical compositions can produce glasses with desired optical and other physical properties under industrial conditions. At present these problems can be solved only experimentally and this approach was used in the present work. It was advantageous, however, to use the results of the study of the structure of tellurite glasses for a theoretical consideration of glass formation in tellurite systems. The treatment of experimental data on the dependence of the density and optical constants of tellurite glasses on their chemical composition showed that the methods for the calculation of glass properties described in the literature (the methods of Gilard and Dubrul,[1(b)] Young and Finn,[1(c)] Huggins and Sun,[1(d)] Demkina,[2] and Appen[3] cannot be applied in principle to high-index tellurite glasses. Better methods for the calculation of the density, refractive index, and mean dispersion of these glasses are described in the present paper.

II. Experimental Techniques

The boundaries of the glass-formation region were experimentally determined by preparing glasses in gold crucibles* in batches of 10 g at 700° to 1000°C. The melt was poured into a metal mold at room temperature. The glasses obtained were studied in a polarizing microscope to establish the presence or absence of a crystalline phase.

Glasses selected for further study were produced in batches of 200 g. Melting was done in gold crucibles, using a gold stirrer. The glass melt was poured into a metal mold preheated to 280° to 300°C; castings were first annealed coarsely from this temperature, and then more carefully at a cooling rate of 5° to 8°C/hr. The glass annealing temperatures were determined polarimetrically. The annealing technique used produced specimens nearly free of mechanical stresses as determined by a polarimetric method using a Saint-Armon compensator.

The crystallizability of the glasses was determined by the visual polythermal method and the density was determined by hydrostatically weighing polished specimens in toluene. Refractive indices were measured with autocollimating goniometers at the following wavelengths in the visible spectrum: 656.3, 587.6, 501.6, 486.1, 471.3, and 447.1 nanometers (nm). In some cases optical constants of glasses in the infrared were measured. The transmission of the glasses in the visible part of the spectrum was measured with a spectrophotometer and in the infrared with an infrared spectrometer. The chemical resistance of the glasses to humid atmosphere (hygroscopicity) and weak acid solutions was determined by standard techniques.

Received February 8, 1966; revised copy received July 6, 1966.
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* Stanworth (Ref. 1) has shown that gold is the only refractory metal in which transparent tellurite glasses can be produced without other oxides present.

Table I. Limiting Compositions of Glass-Forming Regions in Binary Tellurite Systems

System	Second component (mole%)	
	Lower limit	Upper limit
TeO_2–Li_2O	17.0 ± 0.3	30 ± 1
TeO_2–Na_2O	10.0 ± 0.5	35 ± 3
TeO_2–K_2O	9.5 ± 0.5	24 ± 1
TeO_2–Rb_2O	8.5 ± 0.5	20 ± 1
TeO_2–Cs_2O	8.0 ± 0.5	15 ± 2
TeO_2–BeO	15.0 ± 1	21 ± 1
TeO_2–MgO*	13.0 ± 1	
TeO_2–CaO	No glasses formed	
TeO_2–SrO*	10.5 ± 0.5	12 ± 1
TeO_2–BaO	10 ± 1	21 ± 3
TeO_2–WO_3	11.2 ± 0.2	33 ± 3
TeO_2–Ta_2O_5	3.1 ± 0.1	9 ± 2
TeO_2–Tl_2O	16.7 ± 0.3	40 ± 5
TeO_2–Sb_2O_3	4.0 ± 0.3	13 ± 3
TeO_2–V_2O_5†	8.5 ± 0.5	40 ± 3
TeO_2–TiO_2 TeO_2–PbO TeO_2–Bi_2O_3	No glasses formed	

* Glasses crystallized readily.
† Red and black glasses.

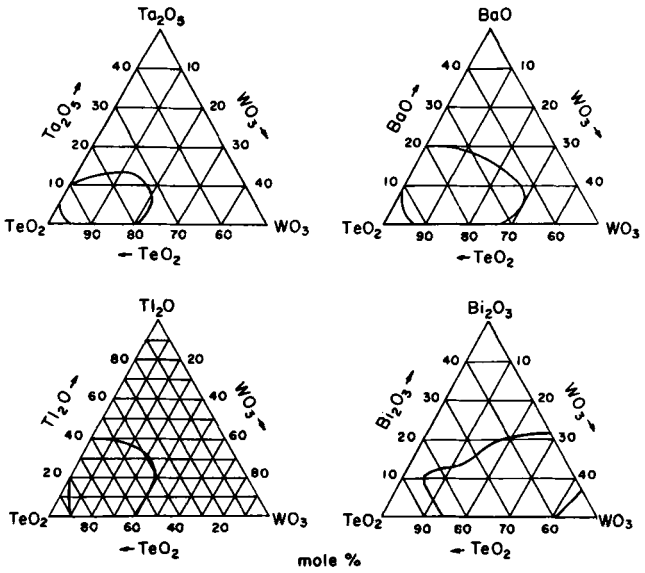

Fig. 1. Regions of glass-forming compositions in ternary tellurite systems.

III. Regions of Glass-Forming Compositions

The results of the determination of the glass-formation regions in the binary tellurite systems studied are presented in Table I. The data given are of limited applicability since they pertain only to the chosen quenching conditions. Experiments have shown, however, that the modifier-poor boundaries of the glass-formation regions are fairly clearly defined. For example, in a binary system with 3.03 mole % Ta_2O_5, complete crystallization of a 10-g cast occurs even with the most refined quenching, whereas glass containing 3.23 mole % Ta_2O_5 can be produced in quantities up to 100 g without any crystallization detectable with a polarizing microscope. The modifier-rich boundaries of glass-forming regions are much less pronounced; compositions lying close to this boundary show a gradual increase in the amount of the crystalline phase in the glass as the content of the modifier oxide increases from 3 to 5 mole %.

The boundaries of the glass-forming regions in the ternary systems studied are shown in Fig. 1. These ternary systems were chosen for study because glasses of high refractive index and low tendency to devitrify can be obtained.

IV. Crystallochemical Interpretation of Glass Formation in Binary Tellurite Systems

The investigation of phase diagrams and of regions of glass formation in binary systems shows that addition of modifier oxides Me_xO_y to pure glass formers (e.g. SiO_2, B_2O_3, and P_2O_5) results in some cases in glass formation (alkali silicate, alkali borate, and alkali phosphate systems), whereas in other cases phase separation occurs, and only with the further addition of Me_xO_y are single-phase melts produced which cool to glasses. Included in the latter group are all binary tellurite systems, among others the alkaline tellurite systems in which phase separation occurs. Tellurium dioxide by itself does not form glass.

Phase separation (immiscibility) may be interpreted as a tendency for the glass former and modifier cations to form their own oxygen coordination polyhedra in accordance with their coordination numbers. This tendency is greater for cations of small radius and high charge, e.g. Be^{2+}, Mg^{2+}, and Al^{3+}. The addition of a modifier oxide results in the breaking of common bonds between the glass former polyhedra because of the oxygen atoms introduced by the oxide. At some compositional limit, however, the formation of separate coordination complexes about each cation will no longer occur as both complexes become compatible. Beyond this limit immiscibility will not occur.

A geometrical consideration of conditions favoring the formation of spatial polyhedral structures which do not produce immiscibility[4] leads to the following expression for the calculation of the number of oxygen ions, N_O, linked to one cation for the limiting composition of the immiscible region:

$$N_O = \frac{s^3 - 6.195\,(r_{Me^{n+}})^3}{17} \qquad (1)$$

s = average separation between the cations Me^{n+} in angstroms.
$r_{Me^{n+}}$ = atomic radius.
6.195 = the ratio of oxygen ion volume to the cube of its radius.
17 = volume of spaces occupied by oxygen ion in close-packed arrangement in A^3.

The principles of crystallochemical interpretation of stratification regions in the phase diagrams of binary oxide systems, developed by Warren and Pincus[5] and recently by Levin and Block,[4] were extended by the author to the calculation of the modifier-poor boundaries of the glass-formation regions in tellurite systems. A necessary and sufficient prerequisite for these calculations is the assumption that in systems having a region of liquid immiscibility, the modifier-rich boundary of immiscibility coincides with the modifier-poor boundary of the glass-formation region. This assumption proved to be well-grounded for systems yielding strongly crystallizing glasses in which quenching only insignificantly affects crystallization.

Brady[6] has shown in an X-ray diffraction study that the network in tellurite glasses is composed of strongly deformed octahedra of TeO_6 having fewer shared edges and apices than the crystal modifications of tellurium dioxide. A reasonable assumption concerning the orientation of modifier ions about the octahedra of TeO_6 is that the ions whose introduction results in the breaking of shared octahedron edges are oriented about oxygen atoms of the same edge. Then the value of s can be calculated from geometrical considerations using the principle of the closest-packed arrangement:

$$s = \sqrt{(l_1 + r_{O^{2-}} + r_{Me^{n+}})^2 - (l_2 + r_{O^{2-}} + r_{Me^{n+}})^2} \qquad (2)$$

l_1, l_2 = interatomic separations Te-O in the octahedra determined by Brady.
$r_{O^{2-}}$, $r_{Me^{n+}}$ = ionic radii (Pauling) of oxygen and Me^{n+}, respectively.

Table II. Calculated and Experimental Values of Modifier Oxide-Poor Regions of Glass Formation in Binary Tellurite Systems

Ion	r_{Me} (A)	s (A)	N_O	Beginning of glass-formation region, mole % of modifier oxide: Calculated	Experimental	Bond strength
Li^+	0.60	5.97	12.03	14.5	17.0	0.167
Na^+	0.95	6.43	15.29	11.9	10.0	0.167
K^+	1.33	6.97	19.43	9.6	9.5	0.125
Rb^+	1.48	7.18	21.23	8.8	8.5	0.08
Cs^+	1.69	7.48	24.00	7.8	7.0	0.08
Cu^+	0.96	6.45	15.43	11.8	11.0*	0.125
Tl^+	1.44	7.13	20.80	9.0	10.8	0.125
Be^{2+}	0.31	5.53	9.83	18.4	11*	0.5; 0.66
Mg^{2+}	0.65	6.01	12.53	14.8	13*	0.33
Ca^{2+}	0.99	6.49	15.72	11.3		0.33; 0.25
Sr^{2+}	1.13	6.69	17.20	11.0	10.5	0.25
Ba^{2+}	1.35	7.00	19.68	9.7	10	0.25
Pb^{2+}	1.21	6.80	18.05	10.0	11.0	0.33
W^{6+}	0.66	6.02	12.59	17.2	11.2	4/4; 1
Ta^{5+}	0.68	6.05	12.78	16.3	3.0	5/6
V^{5+}	0.59	5.92	11.99	16.7	8.5	5/4; 5/6
Ti^{4+}	0.68	6.05	12.78	15.7		4/6
Sb^{3+}	0.90	6.36	14.80	15.0	4.0	0.50
Bi^{3+}	1.08	6.62	16.67	11.6		0.50
Al^{3+}	0.51	5.81	11.35	16.9	6.0*	3/4; 1/2
Cr^{3+}	0.64	6.00	12.47	15.4	2*	0.50
In^{3+}	0.81	6.24	14.00	13.4	8*	0.50
La^{3+}	1.04	6.31	14.40	13.4	5*	0.50

* Data of Baynton, Rawson, and Stanworth (Ref. 8).

Table II lists values calculated from formulas (1) and (2) and experimental values for the modifier-poor boundaries of the glass-formation region in binary tellurite systems. To convert from the values of N_O to the composition of the beginning of the glass-formation region, the following formulas were used:

$$Me_2O \cdot 1/2(N_O - 1/2)TeO_2$$
$$MeO \cdot 1/2(N_O - 1)TeO_2$$
$$Me_2O_3 \cdot 1/2(N_O - 3/2)TeO_2$$
$$MeO_2 \cdot 1/2(N_O - 2)TeO_2$$
$$Me_2O_5 \cdot 1/2(N_O - 5/2)TeO_2$$
$$MeO_3 \cdot 1/2(N_O - 3)TeO_2$$

The calculated values in the table agree fairly well with experimental values for systems containing oxides of monovalent and divalent metals whereas for systems with oxides of multivalent metals agreement is not close.

Pauling's rule concerning electrostatic bond strength (the charge on the ion divided by its coordination number) can be applied to the proposed model. Only ions with electrostatic bond strength less than $+4/9$ can be oriented about the octahedra of TeO_6 close to the oxygen apices sharing the same broken edge. In all the cases where the electrostatic bond strength is 0.33 or less, calculated values agree well with the experimental values (Table II). Typical for ions of multivalent metals with bond strength above $+4/9$ is the formation in the network of the tellurite glasses of their own spatially coordinated polyhedra whose geometry should be studied separately by direct methods of glass structure investigation.

Bobovich and Yakhkind[7] studied Raman spectra of tellurite glasses for a number of binary systems. In particular, it was shown that the spectra of glasses of the tungsten tellurite system possess a band at 930 cm^{-1} which corresponds apparently to completely symmetrical oscillations of WO_4 tetrahedra. Lack of information regarding interatomic separations in the oxygen polyhedra of oxides of multivalent elements, however, precludes at present any extension of the method of calculation of the non-glass-former-poor glass formation boundaries to these cases.

V. Dependence of Glass Density on Composition

The densities of glasses in the systems TeO_2–WO_3, TeO_2–Ta_2O_5, TeO_2–BaO, TeO_2–Na_2O, TeO_2–WO_3–Ta_2O_5, TeO_2–WO_3–BaO, and, to some extent, TeO_2–WO_3–Tl_2O were determined. The compositions of glasses in binary systems were varied in increments of 2 to 3 mole %. The compositions of glasses in ternary systems were located on lines with a constant ratio of two components, the content of the third component being varied in increments of 3 mole %. The densities and the optical constants of some glasses are shown in Tables III and IV.

The densities and molar volumes of glasses in the systems TeO_2–WO_3, TeO_2–BaO, and TeO_2–Na_2O depend linearly on the mole content of the components. The same linear relations are exhibited by glasses in ternary systems. The relation deviates from linearity in the system TeO_2–Ta_2O_5.

The relation between the molar volumes, $\bar{V}$, of binary glasses and their chemical compositions may be represented by the following expressions:

$$\text{system } TeO_2\text{–}WO_3 \qquad \bar{V} = 4.60\, m_{WO_3} + 28.30 \qquad (3)$$
$$\text{system } TeO_2\text{–BaO} \qquad \bar{V} = 1.80\, m_{BaO} + 28.10 \qquad (4)$$
$$\text{system } TeO_2\text{–}Na_2O \qquad \bar{V} = 3.70\, m_{Na_2O} + 28.02 \qquad (5)$$
$$\text{system } TeO_2\text{–}Ta_2O_5 \qquad \bar{V}^2 = 1785.7\, m_{Ta_2O_5} + 806.43 \qquad (6)$$

permitting the calculation of the density of binary glasses with an absolute accuracy of ± 0.01 g/cm³. For densities of 5.8 to 6.2 g/cm³ the relative error of calculations does not exceed 0.2%.

Eqs. (3) through (6) can be used to calculate molar volumes and densities of the oxide components of tellurite glasses in a hypothetical glassy state (see Table V). Using these data, the densities of ternary tellurite glasses can be calculated by an equation implying linear additivity of molar volumes:

$$V = \sum m_i V_i \qquad (7)$$

where m_i = mole fraction of ith component. The discrepancies between the calculated and experimental values of density do not exceed 0.04 g/cm³ (with a relative error of 0.6%).

VI. Dependence of Optical Constants on Composition

Table III lists the optical constants for binary tellurite glasses and Table IV gives those for ternary glasses. For glasses in the systems TeO_2–WO_3–Ta_2O_5 and TeO_2–WO_3–BaO the refractive indices depend linearly on the molar content of the third component along various pseudobinary cuts.

The existing methods for the calculation of optical constants of glasses as functions of their chemical composition (the methods of Gilard and Dubrul,[1(b)] Young and Finn,[1(c)] Huggins and Sun,[1(d)] Demkina,[2] Appen,[3] and others) apply only to multicomponent silicate and borosilicate glasses with silica and boron oxide contents lying within a certain range. The most accurate and widely used method of calculation of optical constants was proposed by Demkina but was not extended even to silicate glasses with a high lead content. The methods proposed by Demkina for calculating constants of high-index tellurite glasses proved inapplicable in principle.

The most rational method of treating data on optical constants of tellurite glasses involves determining ionic refractions of oxygen and quadrivalent tellurium. The Te^{4+} ion is essentially a non-noble gas ion, so that there is no tabulated information on ionic refraction for Te^{4+}.

Having experimental values of refraction for glasses whose composition follows a general formula

$$A\ TeO_2 \cdot B\ Me_xO_y \cdot Z\ Me'_xO_y \qquad (8)$$

where Me_xO_y and Me'_xO_y represent WO_3, Ta_2O_5, or BaO, A and B being constant, and Z varying from glass to glass by amounts small compared to A and B, one can compose a sys-

Table III. Optical Constants and Densities of Binary Tellurite Glasses

Glass No.	Second component (mole %)	Refractive indices 656.3 (C)	587.6 (d)	501.6	486.1 (F)	471.3	447.1	$n_F - n_C$	ν	Density (g/cm³)
					WO_3*					
W 1	11.24	2.178_3	2.199_9	2.241_2	2.251_2	2.263_1	2.283_4	0.0729	16.4	5.806
W 5	15.65	2.173_1	2.194_1	2.235_5	2.245_6	2.256_9	2.277_1	.0725	16.5	5.889
W 7	18.83	2.163_2	2.191_3	2.233_4	2.242_9	2.255_5	2.276_7	.0737	16.2	5.924
W 10	24.92	2.162_4	2.183_8	2.225_2	2.236_2	2.246_7	2.266_7	.0730	16.2	6.025
W 13	35.00	2.150_9	2.172_1	2.213_8	2.223_9	2.235_2	2.256_0	.0730	16.0	6.185
					Ta_2O_5*					
Ta 1	3.2	2.164_9	2.185_4	2.225_1	2.235_4	2.246_8	2.266_0	.0705	16.8	5.747
Ta 3	4.5	2.160_6	2.180_8	2.219_7	2.229_2	2.240_7	2.259_5	.0686	17.2	5.769
Ta 6	8.0	2.157_8	2.177_5	2.215_3	2.225_0	2.236_1	2.254_7	.0672	17.5	5.923
					BaO†					
Ba 7	9.76	2.114_3	2.133_1	2.169_7	2.178_9	2.189_2	2.207_3	.0646	17.5	5.628
Ba 8	16.23	2.076_6	2.094_0	2.125_7	2.136_0	2.145_4	2.161_8	.0597	18.3	5.588
Ba 9	17.21	2.072_6	2.089_3	2.123_1	2.131_3	2.141_1	2.157_7	.0593	18.4	5.581
					B_2O_3†					
B 1	21.0	2.0076	2.0190	2.0332	2.0590			.05137	19.8	4.774
B 2	29.9	1.9717	1.9848	1.9955	2.0173	2.0463		.04559	21.6	4.659
B 3	40.0	1.9487	1.9608	1.9715	1.9924	2.0193		.04373	22.0	4.490

* By preparation.
† By analysis.

Table IV. Optical Constants and Densities of Ternary Tellurite Glasses

Glass No.	Composition (mole %) TeO_2	WO_3	Third component	Density (g/cm³)	n	$n_F - n_C$	ν
			Ta_2O_5				
X1a15	80.90	16.18	2.91	5.927	2.184_2	0.0713	16.6
X1a16	78.61	15.73	5.66	6.006	2.174_5	.0690	17.0
X1a17	76.45	15.29	8.26	6.058	2.167_1	.0678	17.2
X1a18	86.18	10.90	2.91	5.865	2.183_7	.0700	16.9
X1a19	83.75	10.59	5.66	5.925	2.176_3	.0668	17.6
X1a20	81.44	10.30	8.26	5.988	2.173_6	.0676	17.4
X1a21	90.29	6.80	2.91	5.801	2.184_8	.0700	16.9
X1a22	87.73	6.60	5.66	5.874	2.177_4	.0679	17.3
X1a23	85.32	6.42	8.26	5.939	2.168_8	.0669	17.5
X1a24	89.32	2.91	7.77	5.875	2.173_4	.0660	17.8
X1a25	84.40	8.26	7.34	5.943	2.170_0	.0672	17.4
X1a26	80.00	13.04	6.96	6.002	2.172_1	.0756	15.5
X1a27	92.23	2.91	4.85	5.819	2.183_0	.0687	17.2
X1a28	87.15	8.26	4.59	5.919	2.181_8	.0697	17.0
X1a29	82.61	13.04	4.35	5.986	2.172_2	.0712	16.6
21	89.74	1.38	8.88	6.014	2.1578_0	.06409	18.1
23	85.13	6.45	8.42	5.695	2.1687_4	.06655	17.6
			BaO				
X1B34	72.12	24.02	3.85	5.976	2.0725	.06027	17.8
X1B35	69.44	23.15	7.41	5.909	2.143	.0676	16.9
X1B36	66.96	22.32	10.72	6.018	2.1445	.06552	17.5
X1B37	79.36	15.88	4.76	5.895	2.1738	.06918	17.0
X1B39	72.46	14.50	13.04	5.860	2.117	.0626	17.8
X1B40	83.74	10.60	5.66	5.672	2.1507	.06654	17.3
X1B41	79.25	10.04	10.71	5.750	2.1423	.06465	17.7
X1B48	72.47	18.60	8.93	5.946	2.1524	.06645	17.3
X1B55	82.92	10.50	6.58	5.799	2.1664	.06753	17.3
X1B56	78.72	15.74	5.54	5.886	2.1703	.06865	17.0
10	63.77	31.41	4.82	6.152	2.17420	.07123	16.5
13	66.38	24.55	9.07	5.952	2.17696	.07006	16.8
25	79.36	11.54	9.09	5.854	2.17826	.06959	16.9
			Tl_2O				
9	64.16	31.60	4.23	6.143	2.191_6	.07154	16.6
14	68.60	24.86	6.54	6.093	2.1801_4	.07280	16.2
16	79.62	16.54	3.85	6.155	2.169_8	.06175	18.9
27	78.45	10.31	11.24	6.612	2.195_5	.07408	16.1
32	69.99	4.12	16.30	6.536	2.19699	.07914	15.1

Table V. Molar Volumes and Oxide Densities for Hypothetical Glassy State

System	TeO_2 V	ρ	WO_3 V	ρ	BaO V	ρ	Na_2O V	ρ	Ta_2O_5 V	ρ
TeO_2–WO_3	28.30	5.63	32.90	7.05						
TeO_2–BaO	28.10	5.68			29.90	5.13				
TeO_2–Na_2O	28.02	5.70					31.72	1.95		
TeO_2–Ta_2O_5	28.40	5.62							57.8–61.1	7.6–7.2

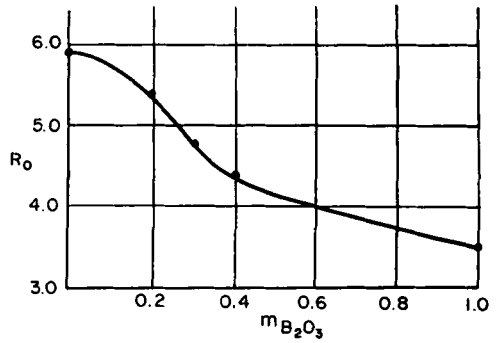

Fig. 2. Refraction of oxygen ion as a function of molar composition in binary borate tellurite glasses.

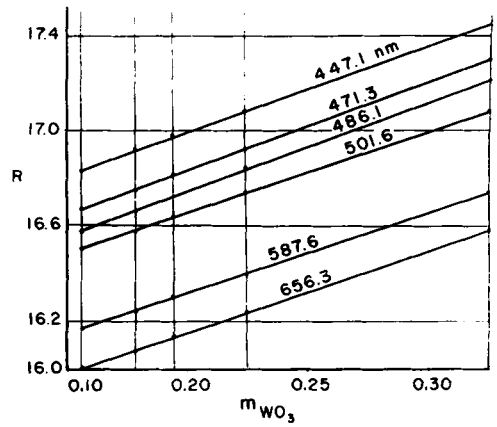

Fig. 3. Molar refractions of glasses in the system TeO_2–WO_3 as a function of composition.

tem of equations with two unknown relating experimental values of refraction for two glasses to ionic refractions of the elements involved. The solution of the system is:

$$R_O = \frac{R_2 - R_1 - 2(Z_2 - Z_1)R_{Ta^{5+}}}{5(Z_2 - Z_1)} \qquad (9)$$

Calculation by formula (9) of oxygen ion refractions for glasses of the system TeO_2–WO_3–Ta_2O_5 differing in composition shows that the refraction of the oxygen ion is constant, does not depend on glass composition, and is, on the average, 6.0 ± 0.4 cm³. The refraction of Te^{4+} ions is also constant and is 4.02 ± 0.07 cm³. Similar relations were obtained for glasses in the system TeO_2–WO_3–BaO, for which the refractions are, respectively, 6.0 and 4.00 cm³.

The independence of refraction of the oxygen ion to glass composition at its high polarizability may be explained as due to the presence in the high-index tellurite glasses of oxides of heavy elements lying close to one another in the Periodic Table. The refractions of oxygen ions in pure oxide components (in cases where the refractive indices of pure oxide components are known) are close to one another (approximately 6). If boron oxide is added to tellurium dioxide, then the refraction of the oxygen ion in such binary glasses decreases from 6 for pure "glassy" tellurium dioxide to 3.5 for glassy boron oxide (see Fig. 2).

Using the values of ionic refractions for oxygen and tellurium, the refractive indices can be calculated for the *d* line of the spectrum with a relative error of 0.6%. To make calculation of refractive indices for other spectral lines possible, a study was made of experimental data for the dependence on composition of molar refractions of glasses for different wavelengths. The molar refractions of binary tungsten- and barium-containing glasses depend linearly on molar composition (Figs. 3 and 4), permitting the determination of molar refractions of the oxides of tellurium, tungsten, tantalum, and barium for different wavelengths (Table VI). Molar refractions for tantalum pentoxide were determined from experimental data for the system TeO_2–WO_3–Ta_2O_5 starting from the values of refractions of tellurium and tungsten oxides given in Table VI and the known analytical composition of ternary tantalum glasses.

Using the single-term version of the Lorentz-Lorenz dispersion formula in the treatment of experimental data on the refraction dispersions of oxides shown in Table VI permitted calculation of dispersion frequencies, ν_i, and numbers of dispersion electrons, p_i. The values are given in Table VII.

Molar refractions of the oxides of tellurium, tungsten, and barium, can be calculated from the values of p_i and ν_i (Table VII). These are in good agreement with values given in Table VI (discrepancies do not exceed ±0.005 cm³). The accuracy of calculation of the refractive indices for binary and ternary tellurite glasses at different wavelengths using the obtained values of p_i and ν_i is, on the average, about ±0.005 (the relative error being about 0.2 to 0.3%).

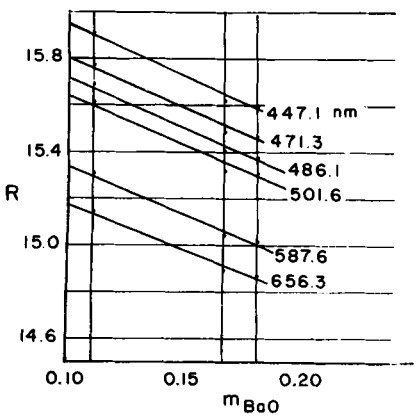

Fig. 4. Molar refractions of glasses in the system TeO_2–BaO as a function of composition.

Table VI. Molar Refractions of Oxides of Tellurium, Tungsten, Tantalum, and Barium for Different Wavelengths

		Molar refractions for wavelengths (nanometers)					
Oxide	System	656.3	587.6	501.6	486.1	471.3	447.1
TeO_2	TeO_2–WO_3	15.72	15.89	16.23	16.30	16.39	16.56
TeO_2	TeO_2–BaO	15.56	15.72	16.03	16.10	16.18	16.32
WO_3	TeO_2–WO_3	18.23	18.40	18.74	18.81	18.90	19.07
BaO	TeO_2–BaO	11.38	11.54	11.84	11.92	12.00	12.14
Ta_2O_5	TeO_2–Ta_2O_5	33.76	33.87	34.40	34.52	34.73	35.07

Table VII. Dispersion Frequencies and Number of Dispersion Electrons for Oxide Components of Binary Tellurite Glasses

Oxide	System*	p_i	$\nu_i \times 10^{-14}$ (sec^{-1})	Wavelength (nm)
TeO_2	TeO_2–WO_3	4.59 ± 0.22	22.22	134.9
TeO_2	TeO_2–BaO	4.95 ± 0.23	25.15	119.2
WO_3	TeO_2–WO_3	6.21 ± 0.53	26.31	113.9
BaO	TeO_2–BaO	2.71 ± 0.09	20.11	149.1

* Refraction was calculated from data for the system.

VII. Spectral Properties

The short wavelength boundary of the transmission region of tellurite glasses lies at 390 to 410 nm. At 450 to 500 nm, the transmittance of glasses reaches a maximum value between 70 and 74%. Losses due to reflection from each surface in the visible region of the spectrum are, on the average, 13 to 15%. An increase in tungsten oxide content causes displacement of the short wavelength transmission boundary to longer wavelengths.

In the infrared region of the spectrum, the tellurite glasses are transparent down to 5.5 micrometers and have a minimum of transmission at 2.8 to 3.6 micrometers due to an absorption band of water. By introducing vanadium pentoxide, color filters are obtained with the initial transmission boundary displaced from the visible region of the spectrum to 1.5 to 2.5 micrometers at a filter thickness of 1 mm.

The coefficient of reflection of high-index tellurite glasses in the visible and infrared regions of the spectrum can be effectively reduced by coating the glasses with silica films since the refractive indices of tellurite glasses are approximately equal to the square of the refractive index of silica.

VIII. Optical Properties and Durability of New Superheavy Flints

As a result of the study of the glass-formation regions, crystallizability, and optical constants of tellurite glasses, chemical compositions of multicomponent weakly crystallizing glasses have been developed with refractive indices of 2.16 to 2.18 and coefficients of dispersion of 16 to 18.*

As an example, the optical constants of one of the glasses developed are as follows:

Wavelength (A)	6563	5893	5875	5461	4861	4358
Line	*C*	*D*	*d*	*e*	*F*	*g*
Refractive index	2.14277	2.16084	2.16141	2.17703	2.20952	2.25306

Mean dispersion $n_F - n_C = 0.06674$

The optical constants (in micrometers) of this glass in the near infrared are:

1.4	1.8	2.0	2.2	2.6	3.0	3.4	3.8
2.0979	2.0821	2.0734	2.0698	2.0663	2.0592	2.0517	2.0432

Glass of this composition can be manufactured on a commercial scale with good reproducibility of the optical constants. It has a high chemical resistance to acids and to humid and corrosive atmospheres. The application of glass for a refractometer was recently described.[9,10]

IX. Summary

(1) Regions of glass formation were determined for binary systems of tellurium dioxide with the oxides of alkalis, alkaline earths, lead, titanium, bismuth, tungsten, tantalum, antimony, and thallium. Corresponding regions were determined for ternary systems with TeO_2 and WO_3 as basic components and Ta_2O_5, BaO, Bi_2O_3, and Tl_2O as third components.

(2) It has been shown that the modifier-poor boundaries of the glass-formation regions in binary tellurite systems including oxides of univalent and bivalent metals can be theoretically calculated on the basis of the crystallochemical interpretation of phase separation in binary oxide systems, using the results of structure determination of tellurite glasses by X-ray diffraction.

(3) The densities of binary and ternary tellurite glasses were measured. Molar volumes of the oxide components were calculated and an empirical method is proposed for the calculation of density using the additive relation between molar volumes and molar composition. The relative error of calculations does not exceed 0.6%.

(4) Optical constants of binary and ternary tellurite glasses as functions of their composition were studied. The refractions of oxygen and tellurium ions for the *d* line of the spectrum were determined as 6 and 4 cm^3, respectively, and do not depend on composition. The molar refractions of oxide components of tellurite glasses for different wavelengths were also determined. A method is proposed for calculating dispersion of tellurite glasses whose relative error does not exceed 0.3%.

(5) Spectral properties of tellurite glasses were studied.

(6) Tellurite glasses with good resistance to devitrification, having refractive indices of 2.16 to 2.18 and coefficients of dispersion from 16 to 18, were produced.

* These glasses are the subject of the author's certificate No. 141,474; of K. S. Evestrop'ev and A. K. Yakhkind, "Glass of High Refractive Index," French Pat. 1,358,696, February 1963; and of the British Patent No. 979,193, March 1963.

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