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URANIUM GLASSES:

II. URANIUM SILICATE GLASSES

by

C. D. Wirkus and D. R. Wilder

AMES LABORATORY
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ABSTRACT

The maximum concentration of uranium dioxide (45 w/o) was determined for silicate glasses. A number of stable glasses were developed. The properties of a typical high-urania-content silicate glass are discussed.

INTRODUCTION

In Uranium Glasses: I. Fundamental Considerations[1] the need for and the possible methods for producing uranium containing glasses were discussed. From a preliminary study of the properties of primary glass-forming oxides only silica and phosphorus pentoxide appeared to be promising bases for uranium glasses. Fortunately, many of the commonly employed glass modifiers and intermediates possess thermal neutron cross sections low enough to make them potentially useful in a glass intended for use in a reactor. This report presents the experimental data

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[1] C. D. Wirkus and D. R. Wilder, IS-107 (1960).

obtained from a study of uranium glasses based on the silicate structure.

COMPOSITION LIMITS OF GLASSES

The limits of composition within which glass formation occurs were determined experimentally for combinations of uranium dioxide, silica, and intermediate and modifying agents in uranium silicate glasses. As a starting point, the formula of a commercial boron-free glass, chosen for simplicity, was altered to include 6.00 w/o UO_2.* Then, additional batches were prepared in which UO_2 and minor additions of other compounds were added at the expense of the original components until the maximum possible quantity of UO_2 tolerable in a stable glass was reached. A total of 33 different compositions were melted (see Table I).

Besides UO_2 and SiO_2, minor additions of a number of other oxides were added to various melts in order to increase the solubility of uranium and enhance the properties of the glasses. Na_2CO_3 was generally added when an alkali oxide was desired, since sodium has the lowest cross section of the group and is readily available at low cost. $CaCO_3$ provided the alkaline earth oxide in most cases; although MgO, which has a lower cross section, probably could have served as well.

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* Number 1, Table I.

Table I

Compositions Melted

No.			Weight Percent					Glass or Crystal	Remarks
	SiO_2	Al_2O_3	CaO	Na_2O	TiO_2	UO_2	Other		
1	66.20	3.50	6.30	12.00		6.00	6.00 K_2O	Glass	Yellow, transparent
2	61.00	2.50	6.00	17.00	3.50	10.00		Glass	Amber, transparent
3	51.00	5.00	6.00	16.00	10.00	12.00		Glass	Brown, transparent
4	41.00	5.00	4.00	15.00	20.00	15.00		Borderline	Cream-brown, opaque
5	48.00	5.00	6.00	15.00	10.00	16.00		Glass	Brown, transparent
6	45.00	5.00	5.00	14.00	10.00	21.00		Glass	Brown, transparent
7	38.00	10.00	5.00	14.00	10.00	23.00		Crystal	
8	43.00	4.00	4.00	13.00	9.00	27.00		Borderline	Glassy with crystalline scum
9	41.00	4.00	3.00	12.00	9.00	31.00		Borderline	Glassy with heavy crystalline scum
10	40.50	5.00	3.00	11.50	9.00	31.00		Crystal	
11	45.50		3.00	11.50	9.00	31.00		Glass	Dark brown. transparent
12	41.00		2.50	11.50	7.00	38.00		Glass	Dark brown, transparent
13	41.00			11.00	7.00	41.00		Borderline	Glassy with crystalline scum
14	45.00			10.00	4.00	41.00		Glass	Dark brown, transparent
15	42.00			9.00	4.00	45.00		Glass	Dark brown
16	40.00			6.00	4.00	50.00		Crystal	
17	50.00	2.00	5.00	13.00		30.00		Glass	Brown
18	46.00	6.00		12.00		36.00		Glass	Brown
19	47.00		3.00	12.00		38.00		Glass	Brown, transparent
20	45.00		2.00	12.00		41.00		Glass	Brown, transparent
21	43.00		2.00	10.00		45.00		Borderline	Few crystal bands in x-ray
22	39.00	4.00	3.00	12.00	6.00	31.00	5.00 ZrO_2	Crystal	
23	45.50		3.00	11.50		31.00	9.00 ZrO_2	Glass	Brown
24	41.00		2.50	11.50		38.00	7.00 ZrO_2	Crystal	
25	44.00		4.00	13.00	9.00	25.00	5.00 Y_2O_3	Glass	Brown
26	43.00		3.50	12.00	9.00	27.50	5.00 Y_2O_3	Glass	Brown
27	41.00		3.00	12.00	9.00	30.00	5.00 Y_2O_3	Glass	Brown
28	40.50		3.00	11.50	9.00	31.00	5.00 Y_2O_3	Glass	Brown
29	41.00		2.50	11.50	7.00	35.00	3.00 Y_2O_3	Glass	Brown
30	41.00			11.00	7.00	38.00	3.00 Y_2O_3	Glass	Brown
31	39.00	5.00	3.00	8.00	9.00	31.00	5.00 P_2O_5	Crystal	
32	39.00	5.00	3.00	8.00	9.00	31.00	5.00 PbO	Crystal	
33	44.00			11.00	8.00	31.00	6.00 PbO	Glass	Brown

Titania proved so useful as an intermediate that it was used in many batches, although titanium does have a rather high cross section. Table II lists thermal neutron absorption cross sections of all the elements present in the oxides used.

PREPARATION OF GLASSES

All the raw materials used in this study were -200 mesh powders. The UO_2 powder was used as received from Mallinckrodt Chemical Works, the only preliminary treatment being the removal of particles coarser than 200 mesh by sieving. It was found that ball milling of the original UO_2 powder easily broke up the coarser particles, but caused the milled material to cling together and ball-up so that later dry mixing with other components was difficult.

Mallinckrodt prepared the UO_2 powder by the cracking of UO_3 with ammonia. Although no analysis of the UO_2 was available, the original UO_3 contained 25 ppm iron and not more than 10 ppm of any other metallic impurity.

The silica used was commercial potter's flint obtained from the Consolidated Feldspar Company. The alumina was No. 38, 220-F Alundum powder produced by the Norton Company. In the interest of better dry mixing, the alumina powder was ball milled in an iron

Table II

Thermal neutron absorption cross sections of elements involved in this study

Element	Cross Section,[7] Barns
Al	0.22
Ca	0.42
K	2.0
Mg	0.059
Na	0.49
O	< 0.0002
P	0.19
Pb	0.17
Si	0.13
Ti	5.8
Y	1.4
Zr	0.18

[7] H. H. Hausner and S. B. Roboff, "Materials for Nuclear Power Reactors", Reinhold Publishing Corporation, New York (1955).

mill, leeched with HCl and washed. The resulting powder was at least as pure as the original product. Titania used in many of the batches was supplied by Titanium Alloy Manufacturing Company as a coarse powder. It too was milled in iron, leeched and washed before use. Yttrium oxide, Y_2O_3, employed in some batches was prepared at the Ames Laboratory. Sodium and calcium carbonates and the remaining oxides were obtained as chemically pure or reagent grade chemicals from Baker and Adamson. Spectrographic analyses confirmed the manufacturer's analyses. The use of reagent grade chemicals was considered permissible since the minor impurities present were judged incapable of altering the results by any serious margin.

Twenty-gram batches were prepared by weighing the components to an accuracy of ± 0.01 gram. Considering the purpose of this study, to fix rather broadly the limits of uranium silicate glass formation, this degree of accuracy was adequate. After weighing, the raw materials were mixed together thoroughly with a mortar and pestle and placed in small unglazed porcelain crucibles for firing.

All the batches were fired in a silicon carbide resistor kiln to a maximum temperature of 1250°C. The small kiln was usually heated to maximum temperature in about six hours. The exact rate of heating was considered unimportant. The maximum temperature was held for 12 hours, which allowed time for adequate fining of all but the most refractory glasses. The power was then turned off and the furnace allowed to cool at its normal rate. Figure 1 shows a typical cooling curve.

The crucibles with their batches were removed from the furnace after the temperature had fallen below 100°C. In most cases the crucibles and the glass or crystalline materials in them had cracked and broken from the stresses of cooling. Pieces of the batch were then separated from the crucibles by chipping and set aside for later tests. The appearance of a typical batch of glass after separation from the crucible is shown in Fig. 2.

Attempts were made to pour some glasses into graphite molds at high temperature, but considerably larger batches were then required. Also, the viscosity of most of the glasses made pouring difficult with the furnace arrangement used. Furthermore, the natural cooling of the glasses in their crucibles provided an opportunity to study the devitrification resistance of the glassy batches.

PROPERTIES

Range of Glass Formation

The chief purpose of this study was to determine the limits of compositions that would form glasses in a system that was principally uranium silicate. By starting with a glass of low uranium content and adding

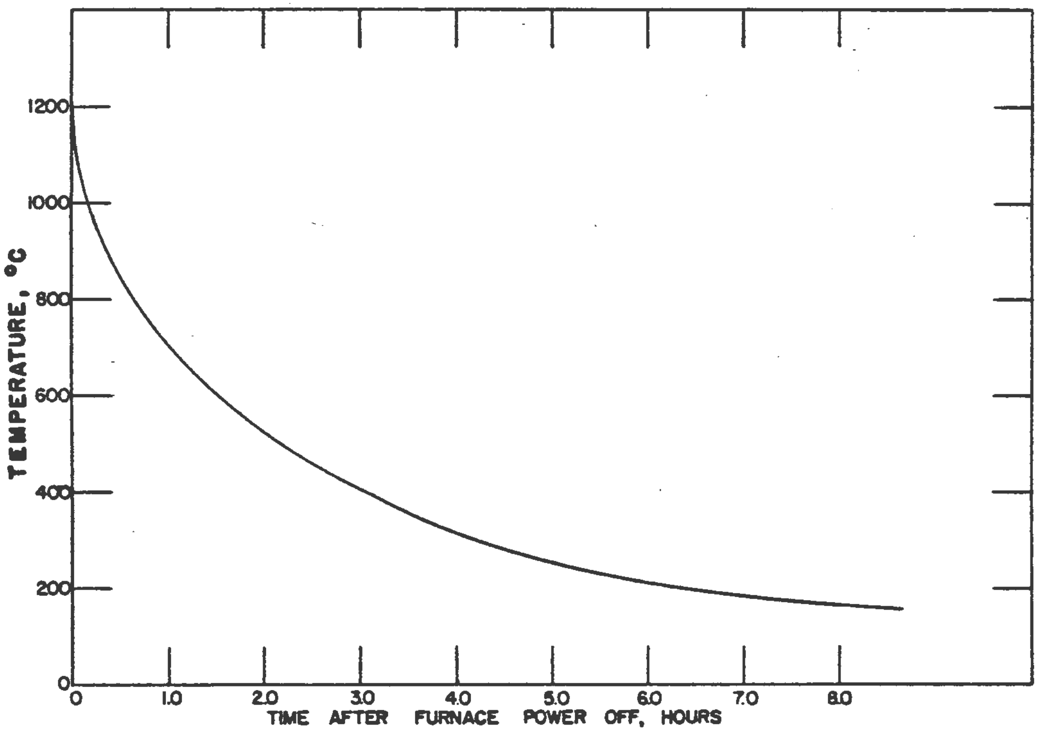

Fig. 1. Cooling curve for glass-melting furnace.

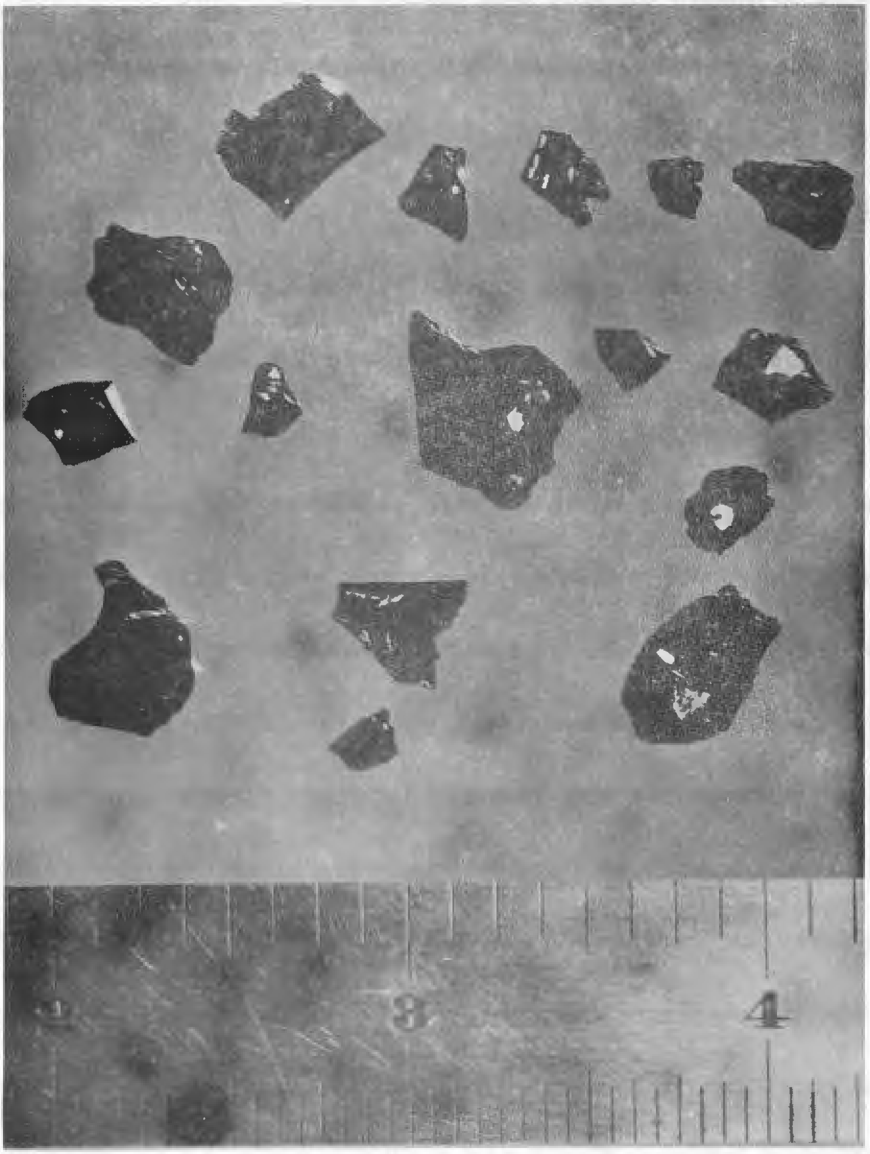

Fig. 2. Appearance of glass lumps after removal from the crucible.

more and more uranium dioxide and minor components to subsequent batches, it was found that glasses with reasonable devitrification resistance could be formed containing up to at least 45 w/o UO_2 and as little as 40 w/o SiO_2.

A glass was judged resistant to devitrification if it remained glassy during normal cooling in the furnace. Figure 1 shows the natural cooling curve of the furnace.

X-ray powder patterns were used to establish the glassiness or crystallinity of the fused batches. In almost every case the appearance of a cooled batch proved to be a reliable indication of its glassiness. Those batches that looked transparent were invariably found to be glassy and those that were opaque and had dull fractures, were usually crystalline. Some batches, such as compositions 8 and 13, were largely glassy but possessed crystalline scums on their surfaces. In all cases batches that formed the crystalline scum were near the borderline between glassy and crystalline melts.

The addition of intermediates and modifiers played an important part in glass formation. It was found that alumina actually was detrimental to the stability of high uranium-content glasses when titania was also present. Stable glasses, such as No. 30, (Table I), which contained Al_2O_3, but not TiO_2, could be formed. Titania in the absence of alumina aided the solubility of uranium dioxide in the glasses. Unfortunately, zirconia was not nearly as effective as titania in this respect, although zirconium has a much more favorable neutron absorption cross section (see Table II).

Na_2O added to melts also aided the incorporation or relatively large amounts of uranium dioxide into stable glasses. However, Na_2O alone was not as effective as a combination of Na_2O and TiO_2 such as employed in composition 15.

Since alumina proved to be an unfavorable addition in the presence of titania, another, larger trivalent ion, Y^{3+} in Y_2O_3, was added to some batches. Yttrium oxide did not have the same detrimental effect on glass formation in titania-containing melts as did alumina.

Good, stable glasses, such as compositions 14 and 15, containing up to 45 w/o urania with silica, titania, and sodium oxide, were prepared. The use of an alkaline earth oxide, such as CaO, as a replacement for some Na_2O or for some UO_2 was possible if about 40 w/o SiO_2 remained to provide the necessary glassy network.

Minor additions, 5 w/o, of P_2O_5 or PbO either had little effect or were detrimental to glass formation. P_2O_5 in a batch yielded a crystalline melt. The effects of PbO are discussed later.

Physical Appearance

All the glasses containing more than 15 w/o UO_2 were brown; below 15 w/o the color lightened to amber and yellow. Inclusion of TiO_2 caused a noticeable darkening of color for a given amount of UO_2. This effect was expected from the observations of Weyl.[2]

Although darkly colored in some cases, all the glasses were transparent except No. 4 which had a brown opal-like appearance. A faint suggestion of crystal lines was found in x-ray powder patterns of composition 4, indicating that it was a borderline glass.

Thin plates of several high uranium-content glasses were ground and polished for microscopic study. Although x-ray patterns showed no crystalline materials present, it still seemed possible that some UO_2 was not dissolving and that particles might be found suspended in the glassy matrix. Furthermore, microscopic examination provided a means for judging the effectiveness of the melting operation by revealing the presence of bubbles in the cooled masses. Some of the more refractory glasses contained many microscopic bubbles; and, of course, all samples were badly strained by cooling in the crucibles. No solid particles of any kind were found in any of the glasses examined.

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[2] W. A. Weyl, "Coloured Glasses", The Society of Glass Technology, Sheffield, England (1951).

Oxidation and Devitrification Resistance

Some indication of the oxidation and devitrification properties of the glasses was provided by the melting and cooling operation. All the compositions listed as glasses in Table I retained their glassy nature during the cooling period indicated in Fig. 1. Any that might have been glassy if quenched, but crystalline when cooled more slowly were considered crystalline.

One glass, No. 14, a typical high-uranium content glass, was studied more carefully for oxidation and devitrification resistance. Lumps of the glass were held for eight hours at each of the following temperatures: 220°C, 380°C, 670°C and 800°C, and for 30 hours at 550°C. No changes were observed except in the 800°C-test. After this treatment the edges of the glass samples had rounded somewhat and minor slumping had occurred (see Fig. 3). Very light surface scums on some glass lumps from the 800° test were also observed; and two very faint crystal lines were visible on x-ray powder patterns of the sample after treatment. Devitrification then occurred very slowly at 800°C.

X-ray powder patterns of the glass after each of the other heat treatments revealed that no crystallization had occurred.

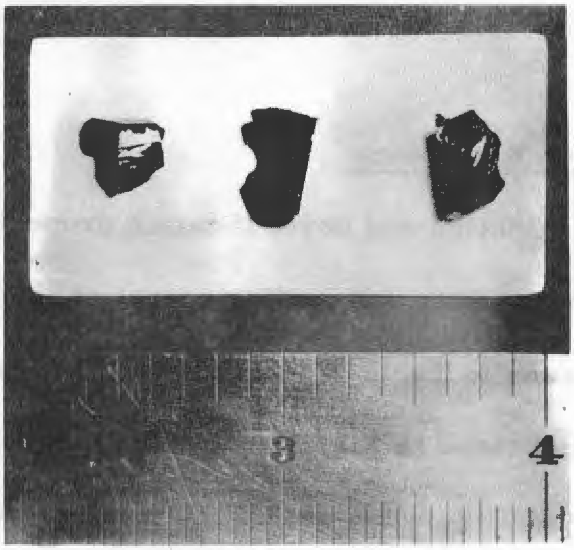

Fig. 3a. Prior to 800°C cycle.

Fig. 3b. After 800°C cycle.

Solubility

The solubility of a typical high uranium-content glass, composition 14, in contact with seven liquids was determined. Of the seven, boiling water, hydrochloric acid, nitric acid, sulfuric acid, hydrofluoric acid, aqua regia, and sodium hydroxide, only hydrofluoric acid caused any noticeable change in the 40-100 mesh particles. Both dilute and concentrated hydrofluoric acid dissolved the glass completely.

The boiling water test was made by boiling particles of No. 14 in distilled water for eight hours. The boiling flask was fitted with a condenser that returned evaporated water to the flask to maintain constant volume throughout the test. After eight hours the liquid was filtered and analyzed colorimetrically for uranium. A uranium content of 0.2 micrograms per ml was present in the water (see Table III). The glass can be regarded as practically insoluble in water. Corundum, which is often considered insoluble, has approximately five times the solubility of this glass.

To provide an indication of the solubility of the glass in other common reagents, 40-100 mesh particles were stirred for 24 hours at room temperature in concentrated solutions of HCl, HNO_3, H_2SO_4, aqua regia and $NaOH$. Portions of liquid were then removed, neutralized, and the neutral solutions evaporated to dryness. The

Table III

Solubility of No. 14 in common reagents

Reagent	Spectrographic Analyses		Colorimetric Uranium Determination
	Boron	Silicon	
Boiling water	No spec. analysis run		0.2 Microgram per ml
NaOH	Not detected*	Not detected*	less than 4 ppm
H_2SO_4	Very weak lines	Weak lines	less than 5 ppm
HNO_3	Not detected#	Not detected#	less than 5 ppm
HCl	Not detected#	Not detected#	less than 4 ppm
Aqua Regia	Not detected#	Not detected#	11 ppm
HF	Dissolved the glass completely		------

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* Detection limit; 300-500 ppm

Detection limit; 50 ppm

crystals resulting from these evaporations were analyzed spectrographically for silicon and boron, and the results are listed in Table III. None of the three elements were detected in the remains of any of the solutions except sulfuric acid. No standards were available for estimating the limits of detection for silicon and boron. However, it was conservatively estimated that 50 ppm of either of the elements in the crystals from the aqua regia, HCl or HNO_3 would have been detected, and that 300-500 ppm of either could have been detected in crystals from H_2SO_4 or NaOH.

The spectrographic test for uranium is quite insensitive, so a series of thiocyanate colorimetric determinations were made. Results obtained from these determinations are also listed in Table III. With all solutions except aqua regia, and, of course, HF, it should be noted that the solubility of uranium from the glass lay below the value listed. Glass No. 14, then, was quite insoluble in all the reagents tried except HF. It further seems reasonable to assume that other uranium silicate glasses near this sample in composition would also have low solubility.

Thermal Expansion

The coefficient of thermal expansion of glass No. 14 was determined with an apparatus similar to the devices described by other investigators.[3]

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[3] (a) T. S. Shevlin and A. R. Blackburn, J. Am. Cer. Soc., 32, 363-366 (1949).

(b) O. J. Whittemore, Jr., and N. N. Ault, J. Am. Cer. Soc., 39, 443-444 (1956).

The ends of a 2-inch cylinder of this glass were ground to points and the sample was placed horizontally on a prefired bed of powdered silica in a small silicon carbide resistance furnace. Changes in length of the sample with changes in temperature were measured by sighting a calibrated traveling telescope first on one end of the sample and then on the other through two holes passing through the furnace. A large number of determinations were averaged, fixing the coefficient of linear thermal expansion of this glass at $6.8 \pm 0.1 \times 10^{-6}$ °C^{-1} in the range of 0-550°C. This value can be compared to 3.3×10^{-6} for Pyrex and 10.8×10^{-6} for American plate glass.

Density

The densities of 14 glasses from various parts of the system were determined by the water displacement method and the results are shown in Table IV. The density determinations were made on a group of relatively small lumps of each glass and with glasses thought to be largely free of microscopic bubbles. Nevertheless, some densities reported here may be slightly low because of tiny undetected, unavoidable bubbles. Densities of the glasses tested ranged from 2.94 for glass No. 5 with 16% UO_2 to 3.56 gm/cc for No. 15 which contained 45% UO_2.

DISCUSSION

A reasonably high percentage of a good glassformer is obviously required in forming any stable glassy network. Silica, the glass-forming agent in this study, was necessary in amount of 40 w/o or more in all the glasses prepared. In a typical glass containing 41 w/o SiO_2, (No. 19), however, about 52% of the cations present are Si^{4+}, which seems a reasonable number to form the framework for a stable glass.

As much as 45% UO_2 by weight was successfully incorporated into stable glasses. Even at this maximum concentration, only 13.8% of the cations present in the structure were of uranium. As noted in Part I, it is probable that uranium ions could serve either as modifiers or intermediates depending on the environment. If it is assumed that they are present both as modifiers and intermediates in the high-uranium-content glasses, the 13.8% figure is not surprisingly high.

Other investigators[4] found that little reaction occurred between UO_2 and SiO_2 heated together in the absence of other oxides. The chief problem, then, was to alter the primary silica glass network sufficiently that uranium ions could exist in the structure either as

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[4] W. M. Cashin and H. G. Sowman, Knolls Atomic Power Laboratory, Schenectady, New York. AEC Research and Development Report, KAPL-1475 (1956).

modifiers or intermediates or as both. In this case the necessary alteration was accomplished in two different ways. In some glasses, such as Nos. 18, 19 and 20, the silica network was altered by the inclusion of about 15 w/o alkali and alkaline earth oxides, Na_2O and CaO in this case. These glasses contained no oxides that could be considered intermediates with the exception of UO_2 itself.

The use of an auxilliary intermediate, specifically TiO_2, also increased the solubility of UO_2 in the glass. Batch No. 15, which contained 4 w/o TiO_2, remained totally glassy during normal cooling, although it contained 45 w/o UO_2. Number 21, a borderline batch that showed incipient crystallization, also contained 45 w/o UO_2 but no TiO_2. Inclusion of too much TiO_2 was detrimental to the glass probably because the overly weakened silica network was more susceptible to devitrification.

Unfortunately, titanium has a relatively high cross section of 5.8 barns. Therefore, an attempt was made to substitute ZrO_2, which is the next most favorable MO_2 intermediate from an ionic-size standpoint. Batch No. 24 was identical to No. 12 except that ZrO_2 was substituted for TiO_2. The titania-containing batch was glassy, the zirconia batch crystalline. Zr^{4+}, with its slightly larger radius, and uranium dioxide together in the glassy network apparently promote easy devitrification by forming too many centers of high coordination. The tendency, then, is to form a compact, crystalline structure of cations surrounded by more than four oxygens, rather than a glass composed of MO_4 groups.

Alumina was added to uranium silicate glasses with little effect in the absence of titania. Al_2O_3 and TiO_2 together in a batch caused crystallization as expected. It was known that alumina in some titania-containing porcelain enamels promotes the formation of crystals and thereby aids opacity.[5]

Small amounts of Y_2O_3 were added to some batches containing TiO_2 to determine the effects of a larger trivalent cation. Titania and yttria were quite compatible together as illustrated by compositions 28, 29, and 30, which were all glassy. The much larger Y^{3+} ion, then, did not promote devitrification as did Al^{3+}. Yttria additions had another possibly useful effect also; they increased the density of glasses containing 25-35 w/o UO_2 (see Fig. 4). This effect probably resulted from the high charge of Y^{3+}, which caused it to bind more closely to the structure and to draw the open glassy network together to some

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[5] A. Dietzel and R. Boncke, Sprechaal, 75, 342-346; 365-368 (1952). Chem. Abs., 38, 5374 (1944).

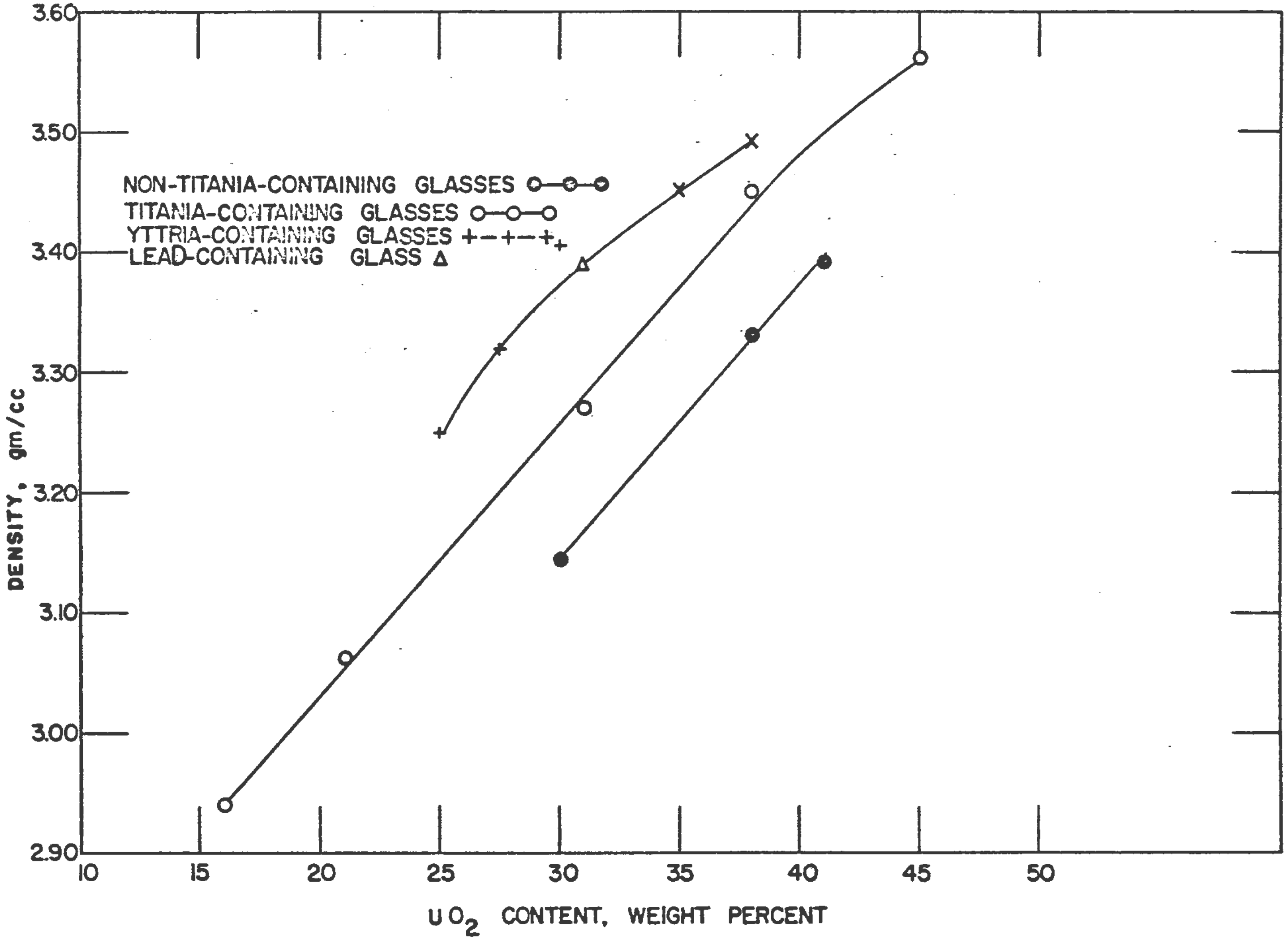

Fig. 4. Density vs. UO_2 content.

extent. Overly compact structures tend to crystallize, so too much Y_2O_3 or other high-charge modifier would be expected to cause loss of stability in the glass. It does not seem possible that Y^{3+} could act as an intermediate because of its size (see Table V).

Minor additions of PbO did not impair glass formation if either Al_2O_3 or TiO_2 was absent. Lead in the glass not only lowered its processing temperature, but also the temperature at which it was usable. Lead oxide also increases the density of the glass, but no more than Y_2O_3 (see Table IV).

As shown in Table III, a typical uranium silicate glass was quite insoluble in all the common reagents considered except HF. Complete solution of the glass occurs readily in HF, so glass fuels could be easily reprocessed with fluoride treatment and subsequent condensation of UF_6 as suggested by Harteck et al.[6]

SUMMARY

Highly stable uranium silicate glasses containing up to 45 w/o UO_2 present as an integral part of the structure can be prepared. Forty percent silica or more is required in these glasses to provide

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[6] P. Harteck, S. Dondes, and J. W. Michener, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, A/Conf. 15/p/440, USA, July 18, 1958.

Table IV

Densities of uranium silicate glasses

Sample	w/o UO_2	Comments	Density, gm/cc
5	16		2.94
6	21		3.06
33	25	5% Y_2O_3	3.25
34	27.5	5% Y_2O_3	3.32
32	30	No TiO_2	3.145
14	30	5% Y_2O_3	3.40
17	31		3.27
31	31	6% PbO	3.39
18	35	3% Y_2O_3	3.45
23	38	No TiO_2	3.33
19	38		3.45
20	38	3% Y_2O_3	3.49
25	41		3.39
28	45		3.56

Table V

Ionic radii of glass components

	Radii, Å - Determined by:			
Ion	Ahrens	Goldschmidt	Pauling	Zachariasen
Al^{3+}	0.51	0.57	0.50	0.45
Ca^{2+}	0.99	1.06	0.99	0.94
K^{+}	1.33	1.33	1.33	1.33
Mg^{2+}	0.67	0.78	0.65	0.65
Na^{+}	0.94	0.98	0.95	0.98
P^{5+}	0.35	0.34	0.34	0.34
Pb^{2+}	1.20	1.32	1.21	--
Pb^{4+}	0.84	0.84	0.84	---
Si^{4+}	0.42	0.39	0.41	0.38
Ti^{4+}	0.68	0.64	0.68	0.60
U^{4+}	0.97	1.05	0.97	0.93
U^{6+}	0.80	---	---	0.83
Y^{3+}	0.92	1.06	0.93	0.88
Zr^{4+}	0.79	0.87	0.80	0.77
O^{2-}		1.32	1.40	1.46

the glassy framework. The remainder of the glass formula should consist of modifiers, such as Na_2O and CaO, and/or intermediates such as TiO_2. Alumina is a suitable intermediate also in the absence of titania. Minor amounts of high-charge modifying ions, such as Y^{3+}, are compatible with TiO_2 in uranium silicate glass and tend to increase the density of the glass.

A glass containing 41 w/o UO_2 and 45 w/o silica had good oxidation and devitrification resistance up to the softening point, was virtually insoluble in all common reagents except HF, had a density of 3.42 gm/cc, and an average thermal expansion coefficient of 6.8×10^{-6} $°C^{-1}$ in the range 0-550°C.