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Uranium glasses III. uranium phosphate glasses

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URANIUM GLASSES
III. URANIUM PHOSPHATE GLASSES

by

C. D. Wirkus and D. R. Wilder

AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.



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IS-267 ✓

Metals, Ceramics and Materials (UC-25)
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Research and Development Report

URANIUM GLASSES

III. URANIUM PHOSPHATE GLASSES

by

C. D. Wirkus and D. R. Wilder

February 1961

Ames Laboratory
at
Iowa State University of Science and Technology
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C. D. Wirkus and D. R. Wilder

Abstract--The maximum concentration of uranium dioxide (40 w/o) was determined for stable, usable phosphate glasses. A number of such glasses were developed and probable structures are suggested. The properties of a typical high-urania-content phosphate glass are discussed and the effects of various intermediates and modifiers are considered.

INTRODUCTION

In Uranium Glasses: I. Fundamental Considerations,¹ the need for and the possible methods of producing uranium-containing glasses were discussed. Two glass-forming oxides, silica and phosphorus pentoxide, were shown to be promising bases for such glasses.

Glass formation based on the uranium silicate system and the properties of silicate glasses was studied and the results presented in Uranium Glasses: II. Uranium Silicate Glasses.² This report, Part III, presents the experimental data obtained from a study of uranium glasses based on the phosphate structure.

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

²C. D. Wirkus and D. R. Wilder, IS-158 (1960).

COMPOSITION LIMITS OF GLASSES

The limits of composition within which glass formation occurs were determined experimentally for combinations of uranium dioxide, phosphorus pentoxide and minor amounts of other oxides. Several batches consisting solely of UO_2 and P_2O_5 were mixed and melted. Alumina, silica, sodium oxide and yttrium oxide were also added singly or in combinations to some batches.

The limit of UO_2 solubility in a glass was considered reached when any additional UO_2 caused the formation of a crystalline mass rather than a glass after melting and cooling in the furnace. Fired glasses were also examined petrographically for undissolved particles of UO_2 .

PREPARATION OF GLASSES

All the raw materials used in this study were -200 mesh powders. The high purity UO_2 used was from the Mallinckrodt Chemical Works and was fully discussed earlier.² To facilitate intimate mixing of the dry ingredients only particles finer than 200 mesh were used.

The silica used was commercial potters flint from the Consolidated Feldspar Company. The alumina was No. 38, 220-F Alundum powder produced by the Norton Company, which, in the interest of better dry mixing, was wet ball milled in an iron mill, leached with HCl and washed.

Baker and Adamson reagent grade dibasic ammonium phosphate was used as the chief source of P_2O_5 . Spectrographic analysis revealed that it contained only very minor impurities in the form of iron, calcium and magnesium plus detectable traces of aluminum, copper and silicon.

No impurity was considered present in quantities large enough to influence glass formation. The ammonium phosphate was supplied in crystalline chunks which were hand ground before use. There was no significance in the choice of ammonium phosphate as a source of P_2O_5 except that the laboratory had an abundant supply. Some other suitable phosphate, such as phosphoric acid, could undoubtedly have been used without altering the results.

In batches which contained Al_2O_3 , $AlPO_4$ was used as the source for all the alumina and part of the phosphorus pentoxide. The $AlPO_4$ was obtained from the Fisher Chemical Company as a purified powder. In spectrographic analyses, it was found to contain trace impurities of calcium, copper, iron, magnesium and silicon compounds. As in the case of the ammonium phosphate, no impurity was considered present in quantities large enough to influence glass formation in any way.

Yttrium oxide employed in some batches was prepared at the Ames Laboratory by ignition of the precipitated oxalate. Sodium carbonate of 99.7% purity from the J. T. Baker Chemical Company was the source of Na_2O used in several compositions.

Test batches calculated to yield 20 grams of solid after melting were placed in unglazed porcelain crucibles and fired, in most cases, to $1250^{\circ}C$ in a silicon carbide resistor kiln. Some refractory mixes were fired as high as $1300^{\circ}C$ in this kiln as noted in Table I. Heating rates for different mixes varied. Compositions containing large percentages of $(NH_4)_2HPO_4$ required a very slow initial heating rate because violent bubbling occurred and would have expelled material from the crucibles

Table I

Compositions Melted

No.	P ₂ O ₅	Al ₂ O ₃	UO ₂	Others	Glassy or Crystalline	Remarks
1	70.00		30.00		Glassy	Light crystalline scum on surface
2	65.00		35.00		Glassy	" " " " "
3	55.00		45.00		Crystalline	High melting
4	72.00	18.00	10.00		Glassy	Light crystalline scum on surface
5	63.00	23.00	14.00		Glassy	" " " " "
6	65.00	15.00	20.00		Glassy	Partial crystalline scum on surface
7	60.00	20.00	20.00		Glassy	Light crystalline scum on surface
8	55.00	25.00	20.00		Composition melts above 1300°C	
9	55.00	20.00	25.00		" " " "	
10	60.00	12.00	28.00		Glassy	No scum nor crystals present
11	65.00	5.00	30.00		Glassy	" " " " "
12	62.00	8.00	30.00		Glassy	" " " " "
13	55.00	10.00	35.00		Glassy	Crystalline scum on surface
14	50.00	15.00	35.00		Composition melts above 1300°C	
15	55.00	5.00	40.00		Glassy	Crystalline scum on surface
16	50.00	8.00	42.00		Crystalline	
17	60.00		28.00	12.00 Y ₂ O ₃	Glassy	Crystalline scum on surface
18	62.00		30.00	8.00 Y ₂ O ₃	Glassy	Very light crystalline scum on surface

Table I, Cont.

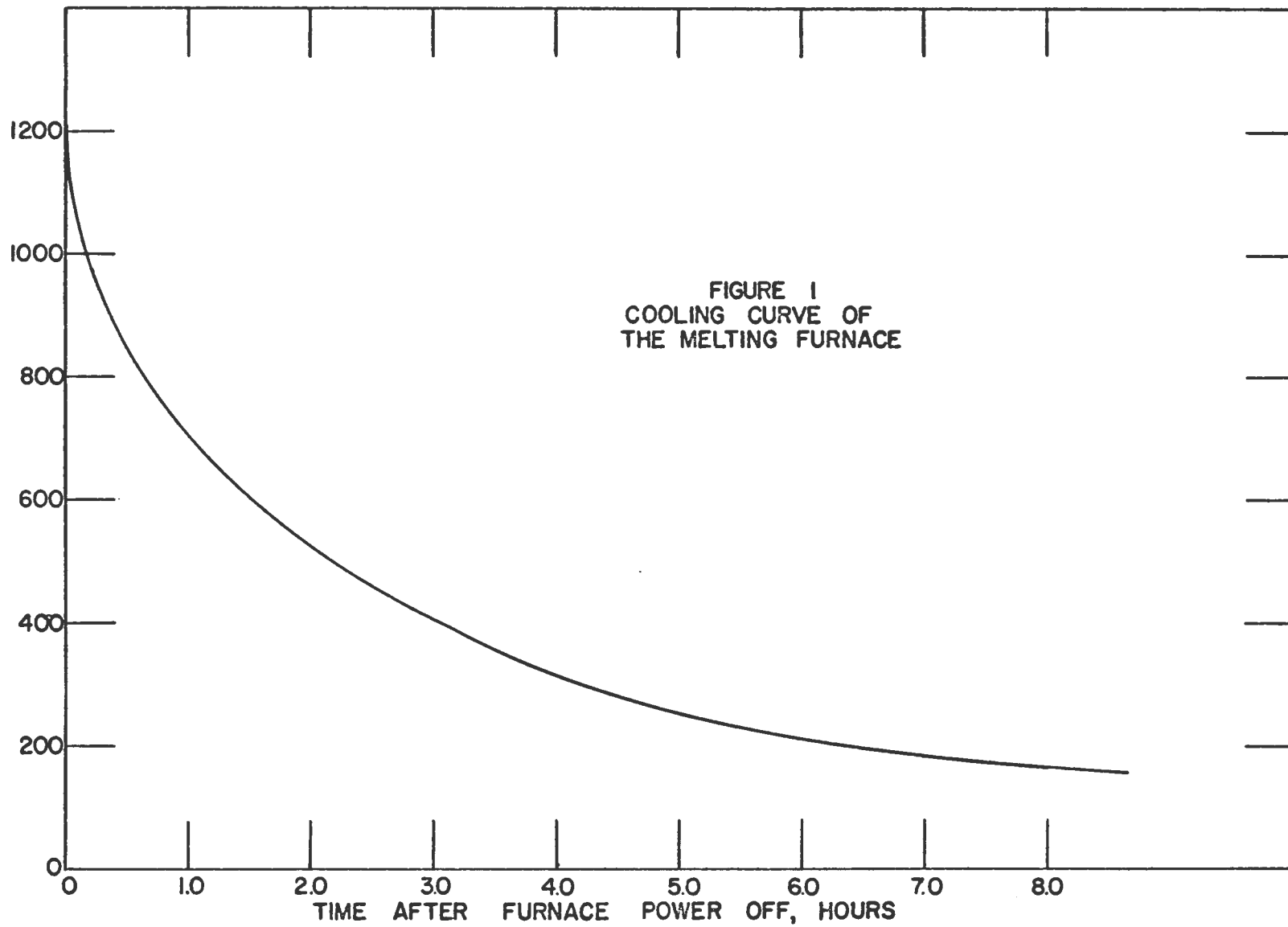
No.	P ₂ O ₅	Al ₂ O ₃	UO ₂	Others	Glassy or Crystalline	Remarks
19	55.00		37.00	8.00 Y ₂ O ₃		Melting was only partial at 1300°C
20	60.00	7.00	28.00	5.00 Na ₂ O	Glassy	No crystalline scum
21	55.00	4.00	35.00	6.00 Na ₂ O		Top phase, glassy; bottom phase, crystalline
22	50.00	5.00	40.00	5.00 Na ₂ O	Crystalline	
23	45.00		35.00	20.00 SiO ₂	Glassy*	
24	45.20	3.80	38.50	12.50 SiO ₂	Glassy*	
25	41.50		40.00	18.50 SiO ₂	Glassy*	
26	25.00		50.00	25.00 SiO ₂	Crystalline*	

*These melts were cooled rapidly as described in the text.

at higher heating rates. Above 900°C bubbling diminished so the temperature could be raised quickly from this point to the maximum where it was held for a period of 12 hours. The power was then turned off and the furnace allowed to cool at its normal rate as shown in Fig. 1. A few silica-bearing batches which were thought to be potential glass formers did not melt completely at 1300°C and these were placed in molybdenum crucibles in a molybdenum tube furnace and refired in helium at $2/3$ atmosphere of pressure. The temperature in the tube furnace was raised at a uniform rate to 1550°C over an hour's time, held there for 15 minutes, and allowed to cool to room temperature in a period of about 30 minutes. Table I shows the compositions studied.

The crucibles and their contents were removed from the furnaces after the temperature had fallen below 100°C and pieces of the batch were separated from the porcelain crucibles by chipping. Batches that were refired in molybdenum were separated by peeling away the 0.003-inch walls of the molybdenum crucibles to leave slugs of melted material.

Pieces of glass about 50 mm long were required for the thermal expansion studies. These samples were prepared by dipping a pyrex tube into a crucible of molten glass at 1200°C and drawing up a rod of the glass, which was then cut and ground to the proper length.



PROPERTIES

Range of Glass Formation

The chief purpose of this study was to produce glasses which were principally uranium phosphate, and to determine the maximum concentration of uranium possible in a devitrification-resistant glass in this system. Most glasses were considered resistant to devitrification if normal cooling in the furnace failed to produce crystallinity. Figure 1 shows the natural rate of cooling of the furnace. As mentioned before, a few silica-containing batches, which failed to melt completely at 1300°C, were fired a second time in molybdenum crucibles in an inert atmosphere, and were cooled much faster; the total cooling time being only about 30 minutes. These rapidly cooled batches are noted as such in Table I. Additional devitrification studies, which will be discussed later, were performed on certain representative glasses. X-ray powder patterns were used to determine the glassiness or crystallinity of the fused batches. Many batches were glassy except for thin, crystalline surface scums.

Alumina in amounts ranging up to 25 w/o was used in many batches to increase the durability and strength of the resulting glasses. More than 25 w/o Al_2O_3 together with more than 20 w/o UO_2 produced a non-glassy, refractory mass. Yttrium oxide was added to two batches to provide an indication of the effects of a trivalent ion larger than Al^{3+} . Y_2O_3 did not extend the range of uranium dioxide solubility nor did it provide any other worthwhile advantages. To some extent, Y_2O_3

interfered with glass formation. Composition No. 18, which is identical with composition No. 12 except for Y_2O_3 substitution for Al_2O_3 , had a crystalline scum which was totally absent from melts formed of composition No. 12.

Five or six percent sodium oxide by weight lowered the firing temperature and the temperature at which the glass could be worked, but did not cause devitrification if the UO_2 content was below 30 w/o. Batch No. 21 which contained 35 w/o UO_2 , separated into two distinct phases. The upper phase was glassy with no scum; the bottom phase, crystalline. The border between phases was abrupt with little evidence of any crystal growth in the glassy region just above the borderline. Spectrographic analyses of the two phases failed to reveal any detectable difference in composition.

Silica additions were neither very helpful nor very detrimental to the uranium phosphate glasses. In general, the silica bearing batches were more refractory and more difficult to fire to homogeneity.

Batches containing up to 40 w/o UO_2 , which were glassy, but had crystalline surface scums, were prepared. A glass containing 30 w/o UO_2 , No. 12 in Table I, was considered the most stable preparation. It formed no scum or crystalline material of any kind during cooling and also had outstanding devitrification resistance in later tests.

Physical Appearance

All the glasses produced that were fired in air were emerald green and transparent, although virtually all of them were so darkly colored

that light was transmitted only through fairly thin sections. All opaque melts were crystalline, even though some of them had a shiny, glassy appearance and exhibited glassy fracture.

Microscopic examinations were made of thin plates of glass which were formed by cutting and polishing sections from lumps of glass removed from the crucibles. Since the glasses were cooled in the confines of the containers, strains were visible in all the plates. Some of the more refractory compositions contained small bubbles indicating that fining was incomplete after 12 hours at 1250-1300°C. Inclusions of solid, opaque particles were observed in some of the silica-containing batches after the initial firing. In reflected light the particles were white and were assumed to be undissolved silica. All the silica-containing batches were filled with small bubbles after the 1250°C firing so microscopic identification of undissolved particles was difficult.

Silica-bearing glasses, which were refired and melted in molybdenum crucibles, were blue in color. Spectroscopic examination indicated the presence of molybdenum throughout the mass of the glass slugs. Solubility of the metal must have been slight, however, since the 0.003-inch walls of the crucibles were not noticeably attacked. Microscopic examination of several plates of the blue, molybdenum-containing glass failed to reveal any solid particles or bubbles.

Oxidation, Devitrification and Melting

All the compositions except Nos. 23-26 listed as glasses in Table I had at least moderate resistance to devitrification and oxygen attack,

since all remained glassy during normal cooling in the furnace. Composition Nos. 23-26, which could not be melted to homogeneous masses in the regular furnace, were cooled much more abruptly as discussed earlier.

Further oxidation and devitrification tests were performed on composition No. 12, one of the most stable glasses in the $\text{UO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ system. Lumps of glass were held for eight hours at 600, 700, 800, 830, and 900°C. The samples held at 900°C fused to hemispheres, but remained shiny and glassy. The sharp edges of the glass samples were rounded slightly after the 800°C test and the lumps were lightly adhered to their porcelain setters. Figure 2 shows glass samples before and after the 830° soaking period. Glass heated to 700°C and below was not noticeably changed. No devitrification and no oxidation occurred in any of the tests.

Composition No. 12 was quite workable at 1200°C. Thermal expansion measurements were made on a small rod about 3/8 inch in diameter and three inches long which was easily drawn from a crucible of molten glass.

Solubility

The solubility of a typical uranium phosphate glass, composition No. 12, in contact with seven liquids was determined.

To indicate the solubility of the glass in boiling water -40+100 mesh particles were boiled in distilled water for eight hours. A condenser on the flask returned evaporated liquid to the container to maintain

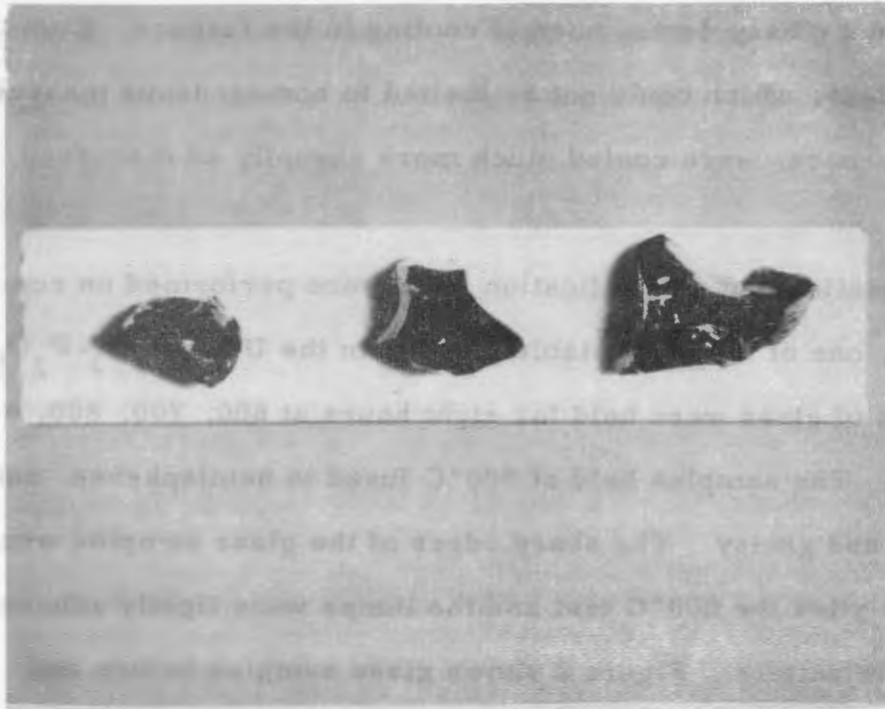


Fig. 2a. Uranium phosphate glass No. 12 prior to 800°C cycle. 2X.

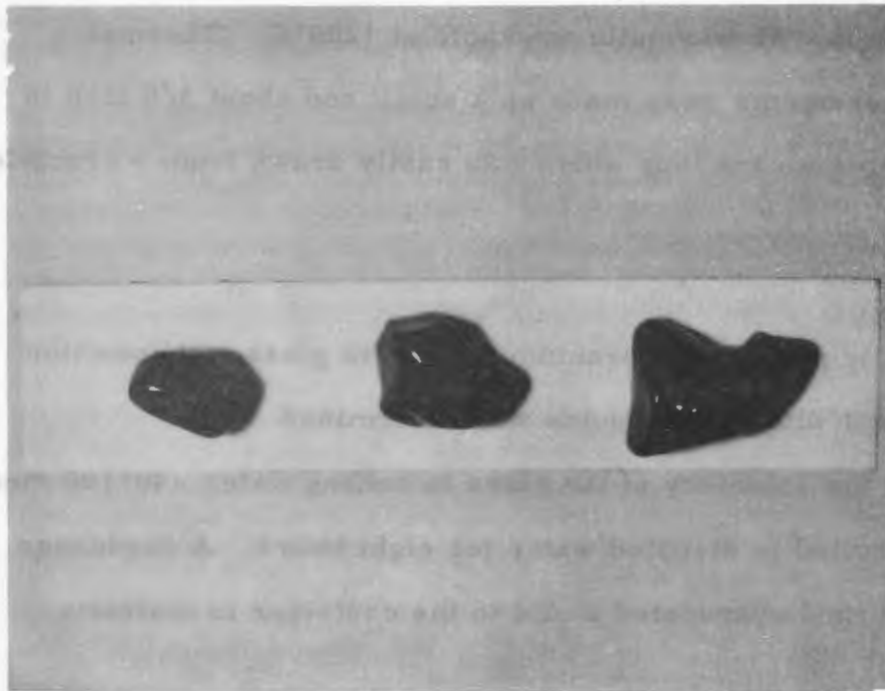


Fig. 2b. Same samples after 830°C cycle. 2X.

a constant volume throughout the test. At the conclusion of the boiling period, the liquid was filtered and analyzed colorimetrically for uranium. A uranium content of 140 micrograms per 100 ml was present in the water (See Table II). This is about 50% above the solubility of corundum and about seven times the solubility of a typical uranium silicate glass. Boiling in water produced no visible change in the glass particles.

The solubility at room temperature of the same glass composition, No. 12, was determined in concentrated solutions of HF, HCl, HNO₃, H₂SO₄, aqua regia and NaOH. -40+100 mesh particles were stirred mechanically for 24 hours in each of the above solvents. Portions of the liquids were then removed and analyzed colorimetrically for uranium. The results are given in Table II.

Table II
Solubility of Uranium Phosphate Glass No. 12

Solvent	U concentration in solvent after test period, micro- grams per 100 ml.
Boiling water	140
Con. HCl	226
Con. H ₂ SO ₄	46
Con. HNO ₃	69
Aqua Regia	149
NaOH Soln.	406

Forty-eight percent hydrofluoric acid removed some uranium from the glass and caused the particles to change in color from emerald green to lighter bluish green. Complete solubility did not occur. Spectrographic analysis of the residue indicated that uranium was the only positive glass component remaining in significant quantities, i. e., likely in the form of uranium tetrafluoride. The glass was soluble in dilute HF solutions. None of the remaining acids had any visible effect on the glass. Sodium hydroxide solutions attacked the particles of glass slowly, but as shown in Table II, uranium was not taken into solution in large quantities. Because reaction of NaOH and glass was slow, another sample of -40+100 mesh particles was soaked in NaOH for 72 hours. This treatment reduced the glass to fine black residue. Spectrographic analysis of this residue indicated that uranium was the major component with only traces of alumina and phosphorus pentoxide present. Given time, NaOH solutions decomposed large chunks of glass. In 10 days a lump 1/2 inch in diameter was completely reduced to fine black residue. X-ray powder patterns of the residue either exhibited no crystalline lines or one or two very faint lines. The dried black residue gradually changed to a khaki color on standing in air.

Since this glass was considered the most stable formed, it seems probable that no other composition in the $\text{UO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ system would have any greater resistance to solvent attack.

Thermal Expansion

The linear coefficient of thermal expansion of glass No. 12 was determined with the apparatus discussed previously.² Numerous

determinations were made to reduce the error inherent in the method. The coefficient of linear thermal expansion was $5.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the range 0-500°C. This value compared with $6.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for a typical uranium silicate glass.

DISCUSSION

All the uranium phosphate glasses of reasonable stability that could be prepared at 1250-1300°C contained at least 55 w/o P_2O_5 . Some of the silica bearing batches which were fired to 1550°C were compounded with as little as 45 w/o P_2O_5 present, but after firing, the uranium content, according to analysis, had diminished five to six percent. Because of the difficulty encountered in analyzing the glasses, no phosphorus determinations were made. However, the drop in UO_2 content could point to an increase in P_2O_5 percentage above 45 w/o in the final melt. Since the analyses for uranium in the glasses were also difficult, the results may have been in error by as much as six percent. In any case, no stable glasses containing less than 45 w/o of the primary glass-maker, P_2O_5 , could be formed. It was thought that some uranium ions might be capable of serving as intermediates in the structure to replace some P^{5+} in network forming positions, and that others could be present as modifiers in the same structure. Under these conditions it might have been possible to prepare glasses with unusually high uranium contents. Probably uranium ions were able to take part in some network-forming MO_4 groups. Even in a glass containing as much as 40 w/o UO_2 with the balance P_2O_5 , the uranium ions would

be outnumbered by P^{5+} by about 5.7 to one. Since P_2O_5 alone does not provide a glassy system with any stability, uranium oxide might have acted as a network former, at least on a limited scale, to produce stable glasses. Because of the size and valence of the uranium ions and from experimental evidence, it seems likely that when the P:U ratio falls below about 5.5, too many centers of high coordination are present and a crystalline material develops during slow cooling. Quenching undoubtedly would produce glassy masses from mixes having higher uranium contents.

As pointed out previously, ¹ phosphate glasses are often more subject to devitrification than silicate glasses because of the valence of the phosphorus ion. The presence of some alumina in the structure increases the stability and durability. Too much alumina, however, lowers the amount of urania that can be incorporated into the glass by creating a network, like pure silica glass, that is an unsuitable environment for large amounts of uranium.

Crystallization of the melts during slow cooling limited the uranium content of the glasses; uranium oxide was quite soluble in all the batches prepared. It is almost certain that glasses containing more uranium could have been formed by quenching. Rapid cooling would have frozen the structure in the glassy state whereas the slow cooling employed permitted structural rearrangement to the more stable crystalline form. Quenched glasses, however, would not have possessed good stability at temperatures near their melting points. Therefore, except for the semiquenched, high-fired silica batches described earlier, no attempt was made to study quenched melts. It should be noted that quenched,

higher uranium content glasses could be useful in certain cases. For example, such a glass could provide more uranium per unit volume and still remain glassy if the temperature of use were below that required for devitrification.

Results of the NaOH solubility measurements raised an interesting question regarding the valence of uranium in the glass. The insoluble residue was black immediately following soaking in the NaOH solution, but changed gradually to khaki on standing several days. Oxidation of the powder was the probable cause of the change. Analytical determinations of the $U^{+4}:U^{+6}$ ratios of the residue before and after storage in air indicated that the material gained in U^{+6} upon standing. However, these analytical results must be viewed with caution, since the presence of foreign oxides interfered somewhat with the determination. If oxidation of the residue did occur, as seems probable, then at least some of the uranium in the glasses must have been present as U^{+4} ions, since it is highly unlikely that NaOH treatment caused reduction of uranium. Uranium is probably tied up in the glass, however, as a combination and specific conclusions cannot be drawn at this time. Work is continuing on this problem.

Additions of intermediates and modifiers were not especially helpful in the glasses prepared. Alumina was added to most of the batches to provide Al^{3+} ions to combine with the P^{5+} in tetrahedral groups similar to the SiO_4 groups in silicate glasses. It was thought that this would produce a stronger glass which was less subject to devitrification, though possibly containing less uranium for reasons mentioned earlier.

Actually, satisfactory glasses were made containing only UO_2 and P_2O_5 . These glasses were about as devitrification resistant as the alumina containing batches with similar uranium contents.

The effects of sodium oxide in uranium phosphate glasses were not unusual in most respects. A lower temperature melting range was expected and did result with Na_2O additions. The two phases observed in melts of composition No. 21 were separated so cleanly that immiscible liquid formation at high temperatures is suggested. As the liquids cooled, the lower one crystallized and the upper one remained glassy. There must, however, be little tendency for devitrification of the upper phase or the presence of the lower crystalline phase would have brought it about. Spectrographic analyses revealed no detectable differences in the compositions of the two phases, although a slightly higher uranium content in the lower phase might have escaped detection. This would explain the bottom-of-the-crucible position of the crystalline phase, which would result from the presence of the added content of the uranium.

The use of another primary glass former, SiO_2 , with P_2O_5 did not add any worthwhile features to the melts. Silica additions, in general, increased the refractoriness of the glasses somewhat, but lowered their devitrification resistance.

Yttrium oxide, Y_2O_3 , did not have the same compatibility with the uranium phosphate glasses that alumina did. The Y^{3+} ion was probably too large to serve as anything but a modifier, while Al^{3+} could take a more active, network-forming part in the structure.

SUMMARY

Stable, devitrification-resistant, phosphate-based glasses containing up to 40 w/o UO_2 in solution can be prepared. About 55 w/o P_2O_5 was required in these glasses to provide the glassy network. With the exception of alumina, modifiers and intermediates did not prove of any value either in enhancing the properties of the glasses nor in increasing the potential for incorporating large quantities of uranium in the structure. Alumina did not materially effect maximum urania content, but did improve the durability of the glasses.

A glass containing 30 w/o UO_2 , 62 w/o P_2O_5 and 8 w/o Al_2O_3 had good oxidation and devitrification resistance up to the softening point, remained virtually untouched in all common reagents except HF and NaOH solutions, had a density of 3.30 gm/cc and a linear thermal expansion coefficient of $5.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.