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Uranium glasses: I. Fundamental considerations

C. D. Wirkus
Iowa State University

D. R. Wilder
Iowa State University

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URANIUM GLASSES
I. FUNDAMENTAL CONSIDERATIONS
by
C. D. Wirkus and D. R. Wilder
UNCLASSIFIED

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URANIUM GLASSES
I. FUNDAMENTAL CONSIDERATIONS

by

C. D. Wirkus and D. R. Wilder

February 1960

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at
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URANIUM GLASSES

I. FUNDAMENTAL CONSIDERATIONS*

C. D. Wirkus and D. R. Wilder

Abstract—The principles involved in forming glasses containing uranium are discussed. Materials having low thermal neutron cross sections that could be useful components in a uranium glass are listed and their properties are discussed.

INTRODUCTION

The efficiency of any reactor as a power-producer can be improved by increasing operating temperatures. It is well known that material properties are limiting the temperatures which may be tolerated in nuclear reactors.

To be specific, a nuclear fuel should have a high melting point and good thermal shock resistance to withstand the imposed thermal stresses. It should have good chemical durability under the conditions of operation, and should lend itself to reprocessing.

To date no fuel form has approached perfection; all have lacked some desirable properties and compromises have been necessary. Elements composed solely of fissionable metals, in general, lack the stability required for high temperature operation. $\text{UO}_2$ or mixed oxides of $\text{UO}_2$ and $\text{PuO}_2$ are stable at high temperatures only if they are

*The first of three papers to be presented on Uranium Glasses.
protected from oxidation. Moreover, these oxides conduct heat poorly, so clad elements must have large surface areas in contact with coolant for adequate heat removal.

The properties of present fuel materials must be improved. Glass may find use as a cementing agent or filler to insure intimate contact of oxide fuels with their claddings. To maintain maximum concentration of fissionable material, the glass should contain significant amounts of uranium. Harteck, et al., suggested that a Fiberglas composed of uranium-containing glass fibers coated with aluminum and rolled into plates could be used as a fuel. Elements of this kind should offer outstanding ease of cooling since masses of small-diameter fibers present large surface areas.

Considering the above, it appears there will be need for $\text{UO}_2$-and/or $\text{PuO}_2$-containing glasses in the future. The purpose of this brief review is to consider the logical possibilities of incorporating such oxides into a glassy structure and to determine the approach that should be taken to develop such glasses.

**FUNDAMENTALS**

There are two obvious ways in which uranium may be contained in a glassy structure. Particles of a uranium-containing material can be physically sealed into a glassy matrix. Using 5-10 w/o $\text{UO}_2$ and 90-95 w/o

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(2) P. Harteck and S. Dondes, Nucleonics, 15, 94-98 (1957).
SiO₂, Cashin and Sowman³ prepared a dispersion of UO₂ in a continuous vitreous matrix, which possessed most of the stability of fused silica.

The second method for binding uranium into a glassy structure consists of forming a glass in which uranium ions are chemically part of the network, and occupy either primary glass-forming ion positions or fill "holes" in the structure as the sodium ion does in a sodium silicate glass. This possibility, which will be discussed here, offers certain advantages over imbedment of particles, especially in fiber production.

Zachariasen⁴,⁵ established the requirements which must be satisfied if glasses are to be formed. The accuracy of these requirements for indicating the glass making potential of an oxide has been amply demonstrated.⁶-⁸

The requirements are:

1. Each oxygen ion is linked to no more than two cations.

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2. The oxygen polyhedra share corners with each other, not edges or faces.

3. The number of oxygen atoms surrounding the positive ion must be small.

4. At least three corners in each oxygen polyhedron must be shared with other polyhedra.

Conditions 1 and 2 must be fulfilled or the positions of the polyhedra in relation to each other will be fixed and a repetitive, crystalline structure will result. Condition 3 limits the number of possible glass-formers by the requirement that the positive ion be small and have a low coordination number. Cations with large coordinations surround themselves with more than four oxygen ions forming compact, non-glassy systems. Condition 4 merely states that the network must be continuous in three dimensions.

**Glass-Formers**

Certain oxides of three different types satisfy Zachariasen's requirements and form glassy networks. These types are $M_2O_3$, $MO_2$ and $M_2O_5$.

$M_2O_3$ oxides can form glasses if the oxygens form triangles around each M ion. In combination with other glass-formers, these ions can also participate in tetrahedral groups if proper compensation is made to preserve electroneutrality. Boric oxide, for example, can form $BO_4$ tetrahedra rather than $BO_3$ triangles when added to sodium silicate glasses.  

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Above a certain percentage of boric oxide, however, $\text{BO}_3$ triangles are formed since only a limited concentration of $\text{BO}_4$ units are stable in glass. The $\text{BO}_3$ triangles are possible because of the very small size of the $\text{B}^{3+}$ ion; three oxygens would be unable to surround and shield a larger ion.

The oxides $\text{MO}_2$ and $\text{M}_2\text{O}_5$ can meet Zachariasen's requirements if the oxygens form a tetrahedron around each cation. Of the tetra-valent ions, $\text{Si}^{4+}$ and $\text{Ge}^{4+}$ form glassy networks. The small, highly charged $\text{Si}^{4+}$ ion, in particular, satisfies Zachariasen's requirements to perfection. It forms strong, stable tetrahedra; and is the best glass-former known.

In the $\text{M}_2\text{O}_5$ group of oxides, glass formation is possible if tetrahedral configurations are formed. The $\text{M}_2\text{O}_5$-based glass structures are inherently weaker than silicate glasses because of the valence of the cation. Since tetrahedral groups are the basic units of construction in $\text{M}_2\text{O}_5$ glasses, not all oxygen ions can be bound to two cations, and a looser structure results. For this reason the addition of a small, tri-valent ion such as $\text{Al}^{3+}$ to a phosphate glass greatly strengthens the structure. The aluminum ion with its plus three charge enters the structure, and, in combination with $\text{P}^{5+}$, permits the bonding of more oxygens to two cations. The net result of using a tri- and a penta-valent ion in the same structure is, in this case, a glassy structure of tetrahedra resembling structures formed of $\text{SiO}_4$ groups.

Glass practice and research have demonstrated that $B_2O_3$, $SiO_2$, $GeO_2$, $P_2O_5$, $As_2O_5$, $As_2O_3$ and $Sb_2O_3$ are glass formers and that possibly $ZrO_2$, $Bi_2O_3$ and $V_2O_5$ can also form glassy structures under idealized conditions.\(^{(11)}\)

**Intermediates**

Some oxides that cannot form glasses alone are able to serve as network-formers in a structure consisting chiefly of a better glass-former. For the most part, these are oxides of the same types that are primary glass-formers. They are not primary glass-formers, however, because their cations are too large to have the small coordination required of true glass-formers.

Certain $M_2O_3$ oxides, notably $Al_2O_3$, have cations that are reasonably small, but still too large for the three-fold coordination required for glass formation with an $M_2O_3$ oxide. Alumina, therefore, cannot form glassy networks alone, but the aluminum ion is able to substitute for $Si^{4+}$ in silicate glasses to form tetrahedral groups. Again, some compensation must be made to achieve electroneutrality since the $Al^{3+}$ ion lacks one valence charge of matching the $Si^{4+}$ it replaces. Neutrality is usually accomplished, in practice, by the inclusion of potassium or sodium ions.

$Al_2O_3$ used with $P_2O_5$ in a glass strengthens the structure because trivalent aluminum ions join with $P^{5+}$ and oxygen to form electrically balanced tetrahedral units.

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Intermediates of the $\text{MO}_2$ type take part in glassy networks by forming $\text{MO}_4$ groups that replace some primary glass-forming groups such as $\text{SiO}_4^4$. Although these intermediates ordinarily have coordinations larger than four, they are able to exist with oxygen in tetrahedral arrangements by distorting the structure. Some network weakening naturally results from this distortion. Zirconia and titania are examples of $\text{MO}_2$ intermediates.

Some intermediate oxides, $\text{MO}$ types, never form glasses alone. Again, these oxides substitute for tetrahedral groups in the glass by forming $\text{MO}_4$ units. Those $\text{MO}$ oxides, therefore, that tend to form the necessary $\text{MO}_4$ groups are the oxides which can act as intermediates. BeO and ZnO are examples of this class of intermediates.

**Modifiers**

Oxides used in glass that do not act as network formers, but exist in "holes" or interstices in the structure are known as modifiers. Modifiers consist of the $\text{M}_2\text{O}'$s and the other oxides that have features that make them unsuitable as glass-formers or intermediates.

Modifiers are useful because they permit wide variation in the properties of a glass. Such modifying ions as $\text{Na}^{1+}$ and $\text{Ca}^{2+}$ do not occupy primary glass-forming positions in the network but instead fill holes in the structure. The addition of modifiers to a silica glass weakens the structure because the ratio of oxygen to silicon rises above 2:1, and some oxygens must then be bonded to only one silicon. The strong tetrahedral groups responsible for the properties of pure
silica glass are disrupted and changes occur such as lower softening point and greater thermal expansion. In phosphate glasses the results are much the same; the inherently weaker phosphate structure is made even weaker by the addition of modifiers.

**Uranium in Glass**

Some oxides can act either as intermediates or as modifiers depending on the conditions existing in the glassy melt. It seems probable that uranium forms such an oxide.

The $U^{4+}$ ion, because of its size of 0.97 a.u., and thereby its greater-than-four coordination for oxygen, would have to be classified a network modifier or perhaps a poor intermediate. However, in a glassy environment which has been distorted and weakened by suitable additions of intermediates and/or modifiers, a limited amount of $U^{4+}$ can probably substitute for the better glass-forming ions by forming $UO_4$ groups.

**CHOICE OF MATERIALS AND COMPOSITIONS**

**Primary Glass-Formers**

The basic building unit of any uranium glass must be a good primary glass-former. If the glass is to be used in a reactor in which the chain reaction is maintained with thermal neutrons, absorption of these neutrons by the cation must also be given careful consideration. Oxygen has an extremely low capture cross section, 12 so the resulting

absorption of neutrons by an oxide glass-former will depend almost entirely on the cross section of the cation.

Of the seven primary glass-formers mentioned above, four can be immediately eliminated because of their ability to capture thermal neutrons. Boric oxide is out of the question, of course. Boron, with a cross section of 750 barns, is a valuable control rod element and certainly could not be considered as part of a fissionable or fertile material. The arsenic oxides and Sb$_2$O$_3$ can also be eliminated from consideration on the basis of their high thermal neutron cross sections. Furthermore, it is doubtful if these oxides could provide a suitably stable network for uranium inclusion even if their cross sections were more favorable, since they both form weak glassy structures.

Of the three remaining glass-formers, GeO$_2$ has the least to offer. It has a rather high cross section of 2.2 barns and is considerably more expensive and scarce than either SiO$_2$ or P$_2$O$_5$. Although Ge$^{4+}$ is like Si$^{4+}$ in some respects, it is larger and is consequently a poorer glass-former.

The two remaining possibilities, SiO$_2$ and P$_2$O$_5$, therefore, should be the logical basic materials for any uranium glass. Of the two, silica is the better, stronger glass-former. Furthermore, high purity silica is inexpensive and plentiful, and appears to be reasonably stable under heavy irradiation. The silicon atom has a satisfactory thermal

neutron cross section of 0.13 barns. However, it must be noted that the
effectiveness of the silica glass structure would probably prevent the entry
of uranium ions in any quantity without the addition of other modifiers or
intermediates.

Phosphorus pentoxide as a basis for uranium glass offers certain
advantages. The phosphate glass structure is inherently weaker than
that of silica for reasons discussed earlier. It should, therefore, provide
a more compatible environment for ions such as uranium. Katz and
Rabinowitch[17] noted that prolonged heating of a phosphoric acid solution
of uranium(IV) phosphate may result in the formation of glasses that
are resistant to chemical action. Baynton, et al.[18] produced small
beads of glass containing considerable amounts of uranium in both the
UO_3-P_2O_5 and Na_2O-UO_3-P_2O_5 systems. Like silicon, phosphorus has
a low cross section (0.19 barns) for thermal neutrons. A uranium
phosphate glass would probably have certain faults because of its weaker
structure. Volatility at high temperatures and excessive solubility could
be serious problems. As in silicate glasses, these structure-dependent
faults might be alleviated to some extent with suitable additives.

Glassy networks composed chiefly of SiO_2 with minor P_2O_5 contents
do not appear promising. The structure of silicate glass offers considerable
resistance to entrance by other network-forming ions, such as P^{5+}.

(17) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium",

(18) P. L. Baynton, H. Rawson and J. E. Stanworth, Nature 178,
910-11 (1956).
Phosphate glasses with minor additions of silica might form a network useful for the inclusion of uranium.

**Intermediates**

The oxides regarded as intermediates are of special interest for use in a uranium glass, for while they alter the structure as do the modifiers, they do so in a different manner. While they weaken or alter the structure by replacing primary glass-formers, they do not disrupt the structure as much as the modifiers.

One of the most important intermediates, as noted earlier, is \( \text{Al}_2\text{O}_3 \). The \( \text{Al}^{3+} \) ion, for reasons already discussed, serves as a glass-former and not as a modifier when added in reasonable quantities to either silicate or phosphate glasses. Addition of alumina to ordinary soda-lime-silica glass increases viscosity and chemical inertness of the glass.

Aluminum has a low cross section and \( \text{Al}_2\text{O}_3 \) is readily available either as the oxide or in various aluminum silicates.

Of the other modifiers, \( \text{TiO}_2 \), \( \text{ZrO}_2 \) and \( \text{ThO}_2 \) are of some interest in considering the formation of a high uranium-content glass. Titania in particular, very probably modifies or weakens the silicate structure to provide a much more satisfactory environment for uranium ions. The \( \text{Ti}^{4+} \) ion, though much larger than \( \text{Si}^{4+} \), substitutes for the silicon ion to produce a distorted, weaker structure. Weyl\(^\text{19}\) noted that \( \text{TiO}_2 \) added to uranium glasses caused the color to intensify and the fluorescence to

decrease, indicating that U$^{4+}$ was favored with TiO$_2$ and that uranium was acting, at least to some extent, as a glass-former rather than as a modifier.

Unfortunately, titanium has a rather high absorption cross section for thermal neutrons (5.8 barns) and could be used only in small amounts in a uranium glass. Possibly zirconia free of hafnia could be used instead to loosen the structure. The zirconium atom has a very low cross section, but is less desirable from the glass-forming standpoint.

Weyl mentioned that ThO$_2$ can also be used to loosen the structure of silicate glasses through the substitution of Th$^{4+}$ for Si$^{4+}$ in the network in the same way that Ti$^{4+}$ substitutes. The thorium ion is larger even than Ti$^{4+}$ so it could be expected to weaken the structure considerably and to promote easy devitrification.

**Modifiers**

Any one member of a group of chemically related modifiers usually yields roughly the same results in a glass as any other member of the same group. In formulating a uranium glass, therefore, modifiers can be chosen from a large number of oxides, and such features as nuclear properties and availability can be given primary consideration.

Of the alkali oxides, sodium oxide, (Na$_2$O), has the most attractive properties. Sodium has the lowest thermal neutron absorption cross section of any of the alkali metals, and Na$_2$O is readily available in the form of sodium carbonate or in other inexpensive compounds.
Several of the alkaline earth oxides are suitable for modifier use in a low cross section glass. CaO, MgO and BeO all have low cross sections for thermal neutron absorption and all are readily available. BeO is much more expensive than the other two, but offers certain advantages over the others in some cases, since the Be$^{4+}$ ion is small and tends to form BeO$_4$ groups. The oxide then acts more as an intermediate than as a typical modifier.

In commercial glasses, modifier-caused changes permit melting and working of the glass at reasonable temperatures, while the somewhat weakened structure remains strong enough to make the glass useful for most ordinary purposes. Although weakening of the structure is undesirable in a uranium glass, it seems likely that any silicate glass will have to be weakened to permit solution of appreciable amounts of uranium.

**SUMMARY AND CONCLUSIONS**

An appraisal of glass-forming principles and of the properties of raw materials for glass suggests two logical solutions to the problem of forming a high-uranium-content glass. These solutions are: 1.) the formation of uranium phosphate glass, and, 2.) the formation of uranium silicate glass.

**Uranium Phosphate Glass**

Two mentions of uranium phosphate glass are found in the literature, 17, 18 but neither gives detailed information regarding a glass suitable for reactor
use. From a theoretical consideration of the factors involved, it seems possible that a uranium phosphate glass composed solely of UO₂ and P₂O₅ could be formed. Addition of some Al₂O₃ should strengthen the glass, but would probably limit the incorporation of UO₂, so a compromise between strength and uranium content would be necessary. Minor SiO₂ additions might also aid in the formation of a glassy network. Inclusion of modifiers, such as sodium or calcium oxides probably would weaken the structure to an objectionable extent. Any phosphate-based glass might possess such undesirable features as volatility during melting, low chemical durability, and excessive solubility. Reprocessing by chemical leaching of uranium from a phosphate glass probably could be accomplished with only simple preliminary treatment.

Uranium Silicate Glass

It is improbable that a glass containing any substantial amount of uranium in solution could be formed from a binary mixture of uranium dioxide and silica. Cashin and Howland²⁰ list a glass prepared by the Owens-Corning Fiberglas Company which contained 9.87% U₃O₈. Probably silicate glasses containing more uranium oxide can be prepared by properly loosening the structure of the glass with TiO₂, ZrO₂, or ThO₂ used with a small amount of Na₂O and/or CaO. Since a relatively large share of the glass formula must be SiO₂ in order to support the glassy network and since the largest possible percentage of uranium is desired, it is obvious that the necessary modifiers and intermediates must be

used sparingly. Probably 50% of the glass should be SiO₂ to provide a good basic network with the remainder of the formula balanced between UO₂ and various modifiers with the UO₂ content being as high as possible.

Reclaiming uranium from the spent glass should be possible with a relatively simple fluoride treatment and subsequent condensation of UF₆.¹