

Enhancing cerium and plutonium solubility by reduction in borosilicate glass

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Abstract

High-level radioactive wastes produced by spent fuel reprocessing containing fission and activation products as well as actinides are incorporated in a borosilicate glass. To ensure optimum radionuclide containment, the resulting glass must be as homogeneous as possible. Microscopic heterogeneity can arise from various processes including the excess loading of an element above its solubility limit. The current actinide loading limit is 0.4 wt%. Work is in progress to assess the actinide solubility in these glasses, especially for plutonium. Initially the actinides were simulated by lanthanides and hafnium. The results show that trivalent elements (La, Gd) exhibit greater solubility than tetravalent elements (Pu, Hf). Cerium is an interesting element because its oxidation state varies from IV to III depending on the process conditions, such as the temperature and redox potential of the melt. In order to quantify the solubility increase, cerium-doped glass samples were melted under reducing conditions by adding a reducing agent. The solubility observed at 1473 K increased significantly from 0.95 to 13.00 wt%. Several reducing compounds have been tested. This paper deals with this study and the application to reduce Pu(IV) to Pu(III). The reduction state was characterized by X-ray absorption spectroscopy (XANES) for plutonium and by chemical analysis for cerium. The material homogeneity was verified by optical and scanning electron microscopy. Preliminary findings concerning the reduction of Pu-doped glasses fabricated in hot cells are also discussed. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

In France, very high-level waste containing fission products, activation products and actinides (residual U and Pu together with minor actinides)

arising from spent fuel reprocessing is currently immobilized in 'R7T7' glass. The plutonium solubility is limited to 1.5 wt% in this glass composition [1], and plutonium is incorporated mainly at tetravalent oxidation state [2]. The oxidation state significantly affects the solubility: the low solubility of tetravalent plutonium (a few percent in borosilicate glass [3]) increases to more than 25 wt% when reduced to the trivalent state [4]. The influence of the oxidation

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state of uranium on solubility had already been noted by Schreiber [5,6]: the U(VI) solubility is close to 40 wt% UO_2 (uranyl chain structure) while that of the reduced U(IV) does not exceed 9 wt%. Recent findings obtained using lanthanide elements as actinide surrogates have confirmed that these elements (La, Gd) exhibit greater solubility than tetravalent elements [1] irrespective of all other parameters. Cerium, with two stable trivalent and tetravalent oxidation states in the glass depending on the melting conditions, was used in this study as a surrogate for plutonium. First, we determined suitable redox conditions for shifting the oxidation–reduction equilibrium of a multivalent species by modifying the redox potential of the cerium glass melt. The experimental protocol was then applied to the synthesis of reduced plutonium-bearing glass to increase its solubility and to obtain basic data on plutonium loading – and, by extension, on the solubility of trivalent actinides in borosilicate glass.

2. Experimental protocol

2.1. Glass fabrication

We opted to test a simplified borosilicate glass composition based on the industrial glass formulation containing the following elements (wt%): SiO_2 58.84; B_2O_3 18.15; Na_2O 7.00; Al_2O_3 4.28; CaO 5.23; Li_2O 2.56; ZnO 3.24; ZrO_2 0.7. The objective was to obtain a composition representative of the glass behavior, but containing no multivalent transition elements (Cr, Fe, etc.) that could have undesirable effects when modifying the redox equilibria. Zirconium oxide was systematically removed from the composition of Pu-doped active glass specimens to avoid any interference between these two elements when analyzing the absorption spectra.

The glass specimens were melted in zirconia or platinum crucibles from oxide, nitrate or carbonate precursors under reducing conditions obtained by

adding an optimized quantity of reducing agent (Fig. 1) in an argon-scavenged furnace. Cerium was supplied as CeO_2 powder, ground and screened to 125 μm . Plutonium was added from a nitric acid solution in which plutonium oxide had been dissolved. The mixture was heated and homogenized for 3 h at the melting temperature. The glass was then quenched by controlled cooling in the furnace to prevent crystallization. The Pu-doped active glass specimens were fabricated in a shielded line in the Atalante laboratory complex.

The solubility of an element is defined as the maximum concentration that can be loaded in the glass while maintaining its homogeneity, an essential property of conditioning matrices. It is determined by gradually increasing the element concentration in the glass, and ranges from a low value corresponding to the maximum quantity of element that can be loaded in a homogeneous glass, to a high value at which the first inclusions appear. The matrix homogeneity is characterized by optical microscopy and scanning electron microscopy (SEM) coupled with X-ray microanalysis (EDX). The progress of the surrogate (Ce) reduction reaction was measured by chemical titration and X-ray fluorescence; the plutonium oxidation state in the reduced glass was determined at room temperature by Pu L_{III} -edge XANES fluorescence spectroscopy on the ROBL beamline of the European Synchrotron Radiation Facility (ESRF) and at the LURE facility for plutonium glass melted under oxidizing condition.

2.2. Redox adjustment in the glass

The glass oxidation state has long been adjusted in the glass industry to improve glass refining or coloring by adding coke or sugar. Few studies of oxidation–reduction (redox) reactions in a liquid glass melt have been reported in the literature. The chemistry of oxidation–reduction reactions in

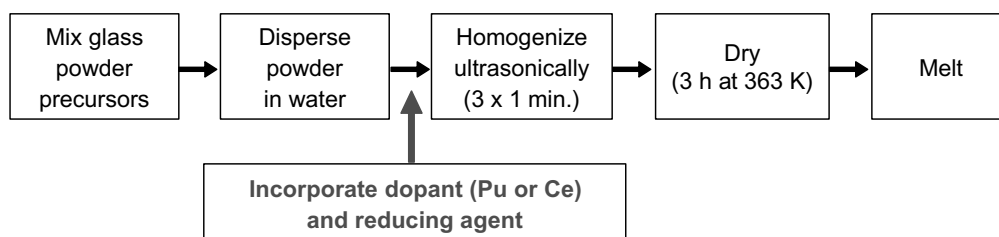
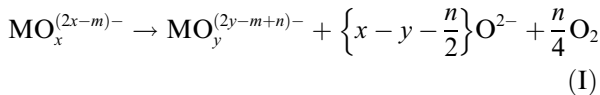


Fig. 1. General glass fabrication flow sheet.

aqueous solution is better known, although the same basic phenomena are involved in both cases [7,8] Molten glass can be described as a solution: the silicate matrix comprising one or more network-forming elements with network-modifying oxides is the solvent, and various additives (dopant, impurities) constitute the solutes. The reference couple in a glass melt is thus not the H^+/H_2 equilibrium of an aqueous solution, but O_2/O^{2-} . The stabilization of an element in the molten glass ‘solvent’ depends mainly on the thermodynamic conditions (T , P), standard enthalpy of the redox equilibrium, and the solvation capacity of the solvent.

The parameters affecting the concentration ratio $M^{m+}/M^{(m-n)+}$ of a redox couple can be identified by equalizing the potentials of the two terms corresponding to the redox couple M and to O_2/O^{2-} equilibrium. The balance reaction is thus:



The Nernst relation of reaction (I) can be expressed at equilibrium when the potential of the redox couple equalizes the potential of the O_2/O^{2-} couple, giving:

$$\begin{aligned} \log \frac{[MO_y^{(2y-m+n)-}]}{[MO_x^{(2x-m)-}]} &= \log \frac{[Red]}{[Ox]} \\ &= \frac{nF}{2.3RT} E_{OM} - \log \beta_M \\ &\quad + \left(y - x + \frac{n}{2}\right) \log a_{O^{2-}} - \frac{n}{4} \log f_{O_2}, \end{aligned} \quad (1)$$

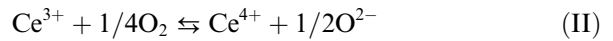
where R is the molar gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$), F is the Faraday constant ($96485.3 \text{ C mol}^{-1}$). E_{OM} is equal to $-\Delta G^\circ/nF$ with ΔG° the standard reaction enthalpy (J mol^{-1}) of reaction (I), β_M is the ratio of the ion activity coefficients of the relevant redox couple, $a_{O^{2-}}$ is the activity of the O^{2-} ions in the glass and f_{O_2} is the oxygen fugacity. Eq. (1) indicates the parameters governing the oxidation state of an element.

- The *oxygen fugacity*: when it increases, the $[Ox]/[Red]$ ratio rises. Eq. (1) shows the $n/4$ dependence of the $\log(f_{O_2})$ and $\log [Ox]/[Red]$ terms. This relation was experimentally verified by Schreiber in borosilicate glass [9].
- The *temperature*: when it rises, the $[Ox]/[Red]$ ratio decreases. This could be explained by the negative sign of the standard enthalpy of the oxidation reaction.

- The *glass basicity*: the concept of basicity is directly related to the concentration of nonbridging oxygen atoms in the glass. The influence of the glass basicity $a_{O^{2-}}$ on the $[Ox]/[Red]$ ratio depends on the sign of the $(y - x + n/2)$ term. For practical purposes, increasing the basicity favors the oxidized states.
- The *glass composition* affects the basicity of the glass and the activity coefficients.

It is thus possible to adjust the oxidation state of a species in a glass matrix by modifying the partial pressure above the melt, the melting temperature, or the basicity of the melt.

In the case of cerium, the modification of the Ce(IV)/Ce(III) ratio can be explained in terms of the cerium oxidation–reduction equilibrium in the glass:



Reaction (II) is exothermic ($\Delta H = -116.3 \text{ kJ mol}^{-1}$); increasing the temperature will thus shift the oxidation–reduction equilibrium toward the reduced form. This has been confirmed experimentally [10]. This investigation of the solubility of multivalent elements Ce and Pu was limited to the effects of adding active species.

3. Results

3.1. Selecting the reducing agent

To reduce the cerium in the test glass, we chose to proceed under flowing neutral gas (argon) by adding a reducing compound to the feed stream. Reducing agents are compounds that decompose in the molten glass, releasing anions likely to become oxidized and thereby reducing the target element. They may also be carbon compounds (coke or graphite) that react with dissolved oxygen and thus modify the redox state of the melt. The reducing species generally used include hydrides (LiH , CaH_2 , $LiAlH_4$), sulfides (Na_2S , CaS , FeS , ZnS), nitrides (Li_3N , Ca_3N_2 , AlN , BN , Si_3N_4), carbides (Al_4C_3 , CaC_2) or simply graphite. The choice of a reducing agent depends to some extent on the ionic nature of the compound reported by Turmel [11]. A sufficient ionicity percentage is necessary to ensure good reactivity. Excessive ionicity can result in sensitivity to moisture, and thus in handling problems. Turmel suggested between 35% and 50% ionicity.

Preliminary tests were carried out with various reducing agents, but some were relatively ineffective.

Table 1
Characteristics of selected reducing agents [12]

Property	AlN	Si ₃ N ₄	B ₄ C
Melting point (K)	2473	2173	2723
Density (g cm ⁻³)	3.26	3.44	2.52
Ionicity (%) [11]	40	28	6

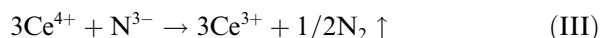
Homogeneity problems were also identified, arising from the difference in density between the glass and the reducing agent, causing the latter to float. The selection criteria identified on the basis of these observations are indicated in Table 1:

- a reducing agent *melting temperature* ensuring proper decomposition in the molten mixture;
- a *density* near that of the glass (2.7 g cm⁻³) to avoid flotation problems;
- an *ionicity* between 30% and 50% for satisfactory reactivity;
- a *cation* compatible with the glass composition.

Three compounds were selected based on these criteria: aluminum and silicon nitrides (AlN, Si₃N₄), and boron carbide (B₄C). Although it does not meet the ionicity criterion, the structure of B₄C provides an ‘electron-rich environment’ that can contribute to the reduction reaction when the boron oxidation state is modified.

After a thorough examination of their reactivity and digestion by the glass, boron carbide and aluminum nitride were excluded. B₄C degrades at low temperatures in contact with nitrates and sodium [13] before the reduction reaction can occur. Aluminum nitride decomposes rapidly in contact with water, losing its reducing power. This is an issue with plutonium, which is supplied in a nitric acid solution. Silicon nitride was selected during preliminary testing to investigate the solubility of Ce(III) versus the melting temperature. The required quantity of reducing agent *R* (mass of reducing agent/

mass of Ce₂O₃ to be reduced) was determined arbitrarily with reference to the following reaction:



Cerium reduction in the glass was not obtained with the theoretical *R* value of 0.07 calculated from the stoichiometric coefficients of reaction (III). Other parameters such as the gas atmosphere or the nature of the crucible may have appreciable effects. The *R* ratio was optimized experimentally by varying the quantity of nitride added to glass samples not exceeding 100 g doped with 5 wt% Ce₂O₃ (Table 2).

The tests yielded an optimized ratio of 0.2 for silicon nitride, used as the reference value for reducing agent calculations in the remainder of this article.

3.2. Cerium reduction

Cerium solubility increases with the melting temperature as its oxidation state approaches that of the reduced species [2,14]. As the reducing agent decomposes, it modifies the redox potential in the molten glass via the oxygen fugacity and shifts the Ce(IV) + e⁻ ↔ Ce(III) equilibrium toward the reduced species, irrespective of the temperature. The solubility of Ce(III) was determined in homogeneous glass (Fig. 2(a)) for melting temperatures between 1373 and 1673 K (Table 3).

Above solubility, microscopic observations revealed heterogeneities of about 10 μm rich in Ce and O, clustered in aggregates at the bottom of the crucible (Fig. 2(b)); these crystals were identified as CeO₂. Another type of crystallization rich in Ca, Si, Ce and O was encountered in highly concentrated glass (Fig. 2(c)–(d)). The size of these inclusions was not sufficient to identify their structure, but an apatitic silicate phase was suspected.

In homogeneous glass, the progress of the cerium reduction reaction can initially be followed easily by

Table 2
Cerium glass homogeneity versus quantity of added Si₃N₄

<i>R</i> (–)	Cerium solubilization	Microscopic characterization	
0.08	Incomplete	Orange glass: Ce(IV)	Crystals at bottom of crucible
0.2	Complete	Colorless glass: Ce(III) A few bubbles	No crystals
0.5	n.d.	Significant foaming	Glass crystallization

R corresponds to the $(m_{\text{Si}_3\text{N}_4})/(m_{\text{Ce}_2\text{O}_3})$ mass ratio.

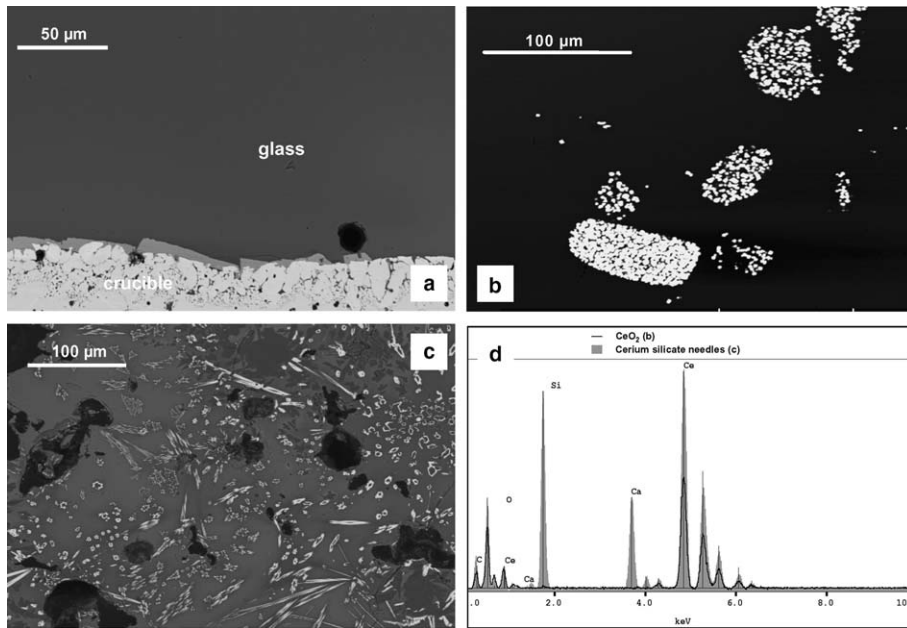


Fig. 2. SEM micrographic images of homogeneous reduced glass containing 13 wt% Ce_2O_3 (a) and inclusions observed above the solubility limits: (b) CeO_2 , (c) cerium silicate needles and (d) corresponding EDX spectra.

Table 3
Main characteristics of Ce-doped glasses

Melting conditions		R (–)	Solubility limits [Ce_2O_3] (wt%)	$m_{\text{Ce(III)}}/m_{\text{Ce total}}$ (%)
T (K)	Atmosphere			
1373	Ar	0.20	10.00 ^a –11.00 ^b	99.8 ± 0.2
1373	Air [14]	0	0.00 ^a –0.25 ^b	53.8 ± 0.6
1473	Ar	0.20	13.00 ^a –14.50 ^b	99.3 ± 0.2
1473	Air [14]	0	0.95 ^a –1.20 ^b	67.7 ± 1.3
1673	Ar	0.20	16.00 ^a –18.00 ^b	99.1 ± 0.2
1673	Air [14]	0	15.00 ^a –16.00 ^b	88.1 ± 0.3

R corresponds to the $(m_{\text{Si}_3\text{N}_4})/(m_{\text{Ce}_2\text{O}_3})$ mass ratio.

^a Homogeneous glass.

^b Glass containing inclusions.

observing the glass coloration. Ce(IV) gives the sample an orange hue, whereas Ce(III) is colorless. The cerium fraction actually reduced as determined by chemical titration in homogeneous glass compositions confirmed virtually complete reduction: more than 99% of the cerium was at the trivalent state (Table 3).

The cerium solubility was thus multiplied by a factor of 20 even at lower temperatures (1373 K) after changing its oxidation state. Another interesting and consistent finding was that the solubilities converge at high temperature toward a limit of 16 wt% Ce_2O_3 in the reduced glass. Reduction was thus beneficial for cerium as a plutonium surrogate.

The observed solubility gain was significant and very promising for the intended application.

3.3. Application to plutonium

Tetravalent plutonium is sparingly soluble in borosilicate glass: 1.5 wt% at 1473 K and 2.5 wt% at 1673 K [1] (Table 4). We therefore undertook to reduce the plutonium before increasing its solubility. A plutonium-bearing glass of standard homogeneous composition (2 wt% PuO_2) was synthesized under reducing conditions (Table 4). This precaution ensured the glass homogeneity and the validity

Table 4
Characteristics of plutonium doped glasses

Samples	PuO_2 content (wt%)	Melting conditions		R (–)	Microstructural observation
		T (K)	atmosphere		
A237	0.85	1473	Ar	0	Homogeneous
A245	1.50	1473	Ar	0	Homogeneous
A247	2.00	1473	Ar	0	Heterogeneous
A251	2.50	1673	Ar	0	Homogeneous
A242	3.00	1673	Ar	0	Heterogeneous
A249	2.00	1673	Ar	0.37	Homogeneous
A252	4.00	1673	Ar	0.56	Homogeneous

R corresponds to the $(m_{\text{Si}_3\text{N}_4})/m_{\text{PuO}_2}$ mass ratio. The Pu solubility limits under oxidizing conditions ($R = 0$) range from 1.50 to 2.00 at 1473 K and 2.50 to 3.00 at 1673 K.

of plutonium oxidation state measurements in the matrix without crystallization of PuO_2 (i.e., Pu(IV)).

XANES analysis was generally used to determine the oxidation state of an element: the energy of the edge depends on the ionization potential of the absorbing atom. In general, the ionization potential increases when the absorber is in a higher oxidation state, the absorption edge shifts toward higher energies with higher oxidation states. The measurement was performed on a perfectly homogeneous sample. The glass absorption spectrum is compared in Fig. 3(a) with reference spectra [15]. The energy peak of the absorption edge in the glass compared with Pu(III) in aqueous solution and Pu(IV) in PuO_2 shows that most of the plutonium was reduced to trivalent oxidation state. The spectrum of the reduced glass is compared with a plutonium-bearing glass fabricated in air under oxidizing conditions, in which tetravalent plutonium was stabilized (Fig. 3(b)). The $\text{Pu(IV)} + e^- \leftrightarrow \text{Pu(III)}$ equilibrium was significantly shifted toward the reduced species. The broad absorption peak of the reduced glass suggests the persistence of a mixture of both oxidation states. It was impossible to quantify the Pu(III)/Pu(IV) ratio, however, not only because of the peak width but also for lack of a trivalent Pu oxide reference. Plutonium thus appears to be slightly more difficult to reduce than its cerium surrogate.

Having demonstrated that plutonium reduction was feasible, we then increased its solubility limits. A glass containing 4 wt% PuO_2 was fabricated under reducing conditions according to the same protocol as above. The quantity of reducing agent was

increased by 50% to shift the redox equilibrium toward trivalent plutonium. Initially colorless, the matrix was colored purple because of the solubilization of plutonium like Pu^{3+} stabilized in perchloric solution. SEM analysis of the glass showed that it was perfectly homogeneous (Fig. 4(a)). Electron probe microanalysis (EPMA) was performed along a vertical line from the bottom to the surface of the sample in 47 μm steps (Fig. 4(b)). The results show that the plutonium distribution was uniform within the matrix and the plutonium content reached on average 3.60 ± 0.06 wt% PuO_2 . The oxidation state of this glass will be examined in the near future.

The solubilities of reduced cerium and plutonium versus the temperature are compared in Fig. 5 with those obtained under standard oxidizing conditions in air without a reducing agent. Note that unlike cerium, the solubility of plutonium does not vary with the melting temperature. The increased cerium solubility was correlated with its thermally activated reduction. For plutonium, the oxidation state does not change with the temperature. This was confirmed in borosilicate glass melted at high temperature (1673 K) [16]. The slight increase in plutonium solubility was related in this case to better dispersion of the precursor and enhanced diffusion of the species with the temperature. Plutonium is thus much more difficult to reduce than cerium, (its commonly used surrogate), which means that the Pu potential is well below that of cerium. From a thermochemical standpoint, cerium as used in this work to develop the reducing process is not a suitable surrogate for plutonium in oxide glasses.

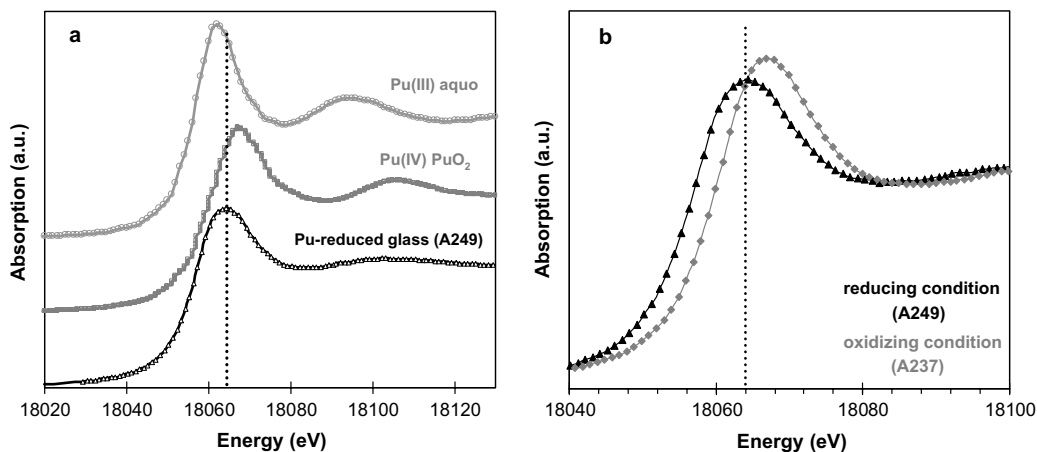


Fig. 3. XANES spectra of a plutonium-doped borosilicate glass (A249) fabricated under reductive conditions compared with reference spectra for Pu(III) in aqueous solution and Pu(IV) in PuO_2 (a) and with plutonium-bearing glass A237 fabricated under oxidizing conditions (b).

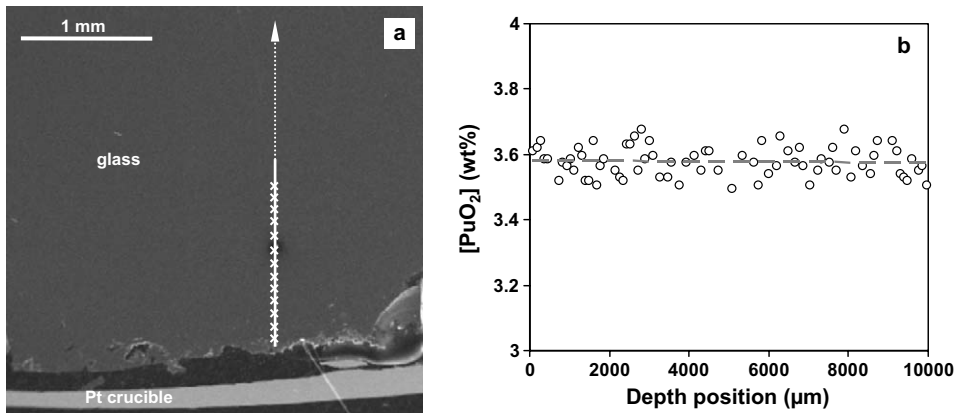


Fig. 4. SEM micrograph of the Pu-doped glass containing 4% PuO₂ (A252). A vertical concentration profile was obtained by EPMA on the entire homogeneous sample (b): the distribution of plutonium was relatively uniform with an average concentration of 3.6% PuO₂.

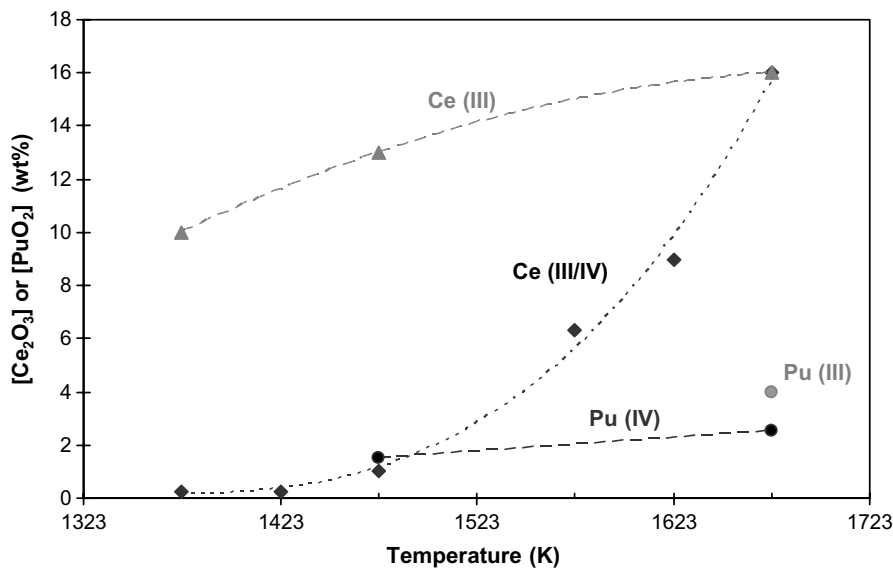


Fig. 5. Cerium and plutonium solubilities versus melting temperature in glass fabricated under reducing conditions and under standard oxidizing conditions.

4. Conclusion and prospects

Reducing cerium by adding a reducing agent to the glass melt significantly increased its solubility. The reduction protocol developed with this surrogate was successfully applied to fabricate reduced plutonium-bearing glass. Characterization showed that the plutonium was mainly reduced to trivalent oxidation state in the borosilicate glass, where tetravalent was its initial stable oxidation state. A homogeneous glass containing 4 wt% PuO₂ was synthesized under these conditions. The Pu solubility was therefore doubled by modifying its oxidation state. The Pu solubility limits must now be determined versus the

temperature in borosilicate glass and according to the Pu(III)/Pu(IV) ratio.

Like lanthanide surrogates such as cerium, trivalent plutonium appears to be more soluble than its tetravalent counterpart. A structural approach to this phenomenon is now in progress and will be discussed in the near future.

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