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Hafnium solubility determination in soda-lime aluminosilicate glass

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Abstract

The solubility of hafnium dioxide (HfO_2), used as an uranium surrogate, is measured in glass melts belonging to the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ systems, under oxidizing and reducing conditions. Two methods have been carried out to determine it and the kinetic factors controlling the HfO_2 dissolution in glass melt have been investigated in order to approach equilibrium. The solubility ranges from 3 to 6.5 mol% HfO_2 in aluminosilicate glasses at temperature between 1250°C and 1400°C, and is not affected by the redox conditions. Conversely, the solubility is modified by the melting temperature and the glass composition. The excess of alkalis or alkaline earths which are not involved in the charge balance of AlO_4 tetrahedrons in the silica network appears to play a significant role. Glass homogeneity is checked by scanning electron microscopy and X-ray diffraction. HfO_2 , HfSiO_4 , $\text{Ca}_2\text{HfSi}_4\text{O}_{12}$, $\text{Na}_4\text{Hf}_2(\text{SiO}_4)_3$ and $\text{Na}_2\text{HfSi}_2\text{O}_7$ are metastable crystals observed in the glass melts. The stability of those crystalline phases mainly depends on the glass composition.

Keywords

Hafnium oxide, solubility, aluminosilicate glass melt, reducing conditions, crystallization.

1 Introduction

1.1 Background

Reprocessing of the spent nuclear fuel generates High Level Waste (HLW) which contains fission products and actinides. To be immobilized, these HLW are incorporated at about 1100°C in a borosilicate glass matrix. In the same way, Intermediate Level Waste (ILW) including both actinides and metals are planned to be confined by a vitrification process. The metallic fraction is melted with the glass melt at a higher temperature, between 1250°C and 1400°C, and the glass melt is expected to incorporate the actinides, uranium and plutonium mainly, in its silicate network. As boron is known to volatilize from borosilicate melts at high temperature [1], aluminosilicate glasses appear as better candidates for that process. Besides, the molten metal phase imposes a strongly reducing environment to the glass melt and thus impacts actinides oxidation state and consequently their solubilities. In highly reducing conditions, U^{IV} and Pu^{III} are the main forms expected in the melt. Plutonium is more soluble in glass melted in reducing conditions (Pu^{III}) [2] while uranium is more soluble in oxidizing conditions (U^{VI}) [3]. Moreover, only few data about uranium solubility in glasses melted in reducing conditions are given in the literature [3-7] and fundamental data on uranium behavior in aluminosilicate glasses have to be investigated in such conditions.

This study presents characteristics of aluminosilicate glasses containing hafnium (Hf^{IV}) which is taken as uranium surrogate [8-11]. Uranium and hafnium are both heavy elements and display quite similar ionic radii for a given coordination number. Preliminary results with hafnium are shown here, before a further study with uranium. The first objective of this work is to study hafnium incorporation into a glass-forming melt under reducing environment and

to optimize the Hf-doped glasses elaboration conditions in order to approach equilibrium. The second objective is to determine hafnium solubility as a function of the melting temperature, the glass composition and the redox conditions. Hafnium crystallization is also investigated.

1.2 State of the art

The thermodynamic solubility of an element in the glass is the maximum concentration of this element that can be loaded in the glass network at a given temperature. To determine it, two methods are commonly used. The first one consists in gradually increasing the amount the element to incorporate in the glass until a heterogeneous phase appears in the system (crystallization or/and demixing) [12]. The second one is embodied in introducing the desired element in excess in the glass and measuring its concentration in the vitreous matrix [13, 14]. That means the saturated glass melt shows lots of heterogeneities. To make a difference between the gradation and the saturation methods, we named the last one the saturation solubility (S_s). The issue of reaching the equilibrium is raised in both cases. To approach equilibrium, the system has to verify several conditions [15], and if not, a conditional solubility (S_c) can be introduced notably for the gradation method [2, 10]. This solubility depends on the experimental conditions used by the authors and it may be lower than the thermodynamic solubility for the gradation method or higher for the saturation technique [16].

Most hafnium solubility studies are focused on borosilicate glasses. Lopez measured conditional solubilities in a borosilicate glass as function of the melting temperature [10]. At 1400°C, hafnium conditional solubility was between 1.2 and 1.5 mol% HfO_2 . Cachia [17] reported a higher conditional solubility at the same temperature, between 1.8 and 2.2 mol% HfO_2 in the same glass by modifying the experimental protocol. In the Na_2O - B_2O_3 system, Res [18] observed that increasing the Na_2O concentration improved the HfO_2 solubility up to 12 mol% HfO_2 at 1400°C for a glass containing 18 mol% Na_2O . Nevertheless, some droplet-like micro-heterogeneities were revealed by SEM in clear glasses. Feng [19] found that hafnium solubility in a sodium boro-aluminosilicate was positively related to the excess of Na_2O relative to Al_2O_3 . At 1450°C, the highest solubility measured in a Na-rich glass was 14.4 mol% HfO_2 . Unfortunately, few data are given about the way of determining that solubility limit. The relationship between the hafnium solubility and glass composition was also investigated by Davis [8]. He demonstrated that the solubility limit of HfO_2 in peralkaline glasses (Na_2O mol% > Al_2O_3 mol%) in the system SiO_2 - Al_2O_3 - B_2O_3 - Na_2O was linearly and positively correlated with the molar $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{Al}_2\text{O}_3)$ ratio. The solubility of HfO_2 in these glasses ranged from 2 to 16 mol% at 1450°C. This “peralkalinity effect” had been alike observed in B-free glass melts for +4 cations (such as Zr^{IV} and Ti^{IV}) [14, 15, 20]. In contrast, the mechanism for HfO_2 dissolution seems to be different in peraluminous glasses (Na_2O mol% < Al_2O_3 mol%). In the peraluminous melts, the HfO_2 measured solubility by Davis [8] is lower than 3 mol% and, B_2O_3 and Al_2O_3 may help to solubilize it. Ellison [20] showed that hafnium solubility decreased in B-free peraluminous melts in the system SiO_2 - Al_2O_3 - Na_2O - K_2O with the SiO_2 content increasing and measured solubility limits lower than 1 mol% HfO_2 in equilibrated liquids at 1400°C. Above the solubility limit, the Hf-bearing crystallized phases were mainly monoclinic hafnia (HfO_2) [8, 9, 18] and occasionally hafnon (HfSiO_4) [10, 20]. All these authors had melted their glasses under oxidizing conditions, namely in air and in Pt-Rh, ZrO_2 or Al_2O_3 crucibles.

2 Experimental and analytical procedures

2.1 General features

Hf solubility was determined in two simplified aluminosilicate glasses based on the industrial glass formulation A and B, A glass containing 22.33 mol% Na₂O while B being sodium free (Table 1) and for two bracketing temperatures (1250°C and 1400°C). Redox conditions during the Hf-doped glasses melting were changed using different types of crucibles and atmospheres. Platinum crucible (Pt-5%Au) and air atmosphere were used for oxidizing conditions, while pure graphite (C_g) or graphite and silicon carbide (C-SiC) crucibles and argon (Ar) atmosphere imposed reducing conditions. The C-SiC crucible (A5/0 Salamander Super, Morgan MMS) is a type of crucible frequently used in the metallurgy field. It is mainly composed of C_g, SiC, a mullite binder (3Al₂O₃-2SiO₂) and some impurities such as Fe₃Si. Ar atmosphere was used to prevent these crucibles from corrosion.

2.2 Glass fabrication

2.2.1 Starting glasses

The A and B glasses (Table 1) were prepared with the following commercial precursors: SiO₂ (*Sifraco*, 0.994); Na₂CO₃ (*Sigma-Aldrich*, 1); CaO (*Aldrich*, 0.999); Al₂O₃ (*Sigma-Aldrich*, 1). For the Na-rich A glass, a decarbonation step was previously performed at 850°C for 6h. Then, the mixed components (≈150 g) were melted at 1400°C for 3h in a platinum crucible (Pt-10%Rh), under air. Glass melts were then poured in stainless steel plate, milled and screened up to 400 μm particle size to be further used as starting glass materials for Hf-doped glasses. Milling was performed in a tungsten carbide (WC) vessel using WC balls (Planetary Ball Mill PM 200).

Hafnium was added as HfO₂ powder (*Alfa Aesar*, 0.999) and mixed with the former glass powders. Three different types of hafnium particle size were used: 15, 70 and 158 μm.

The particle size, expressed as the median value (d₅₀) and size distribution of powders were determined from the volume distribution measured by a laser granulometer (Malvern Mastersizer 3000) in ethanol.

C glass was formed by adding 1.56 mol% HfO₂ to the Na-rich glass (Table 1). This value of 1.56 mol% HfO₂ is a relevant content for the industrial process. Moreover, the hafnium solubility in glass melt should be higher than this value as referenced in paragraph 1.2.

Table 1

Targeted chemical compositions of main glasses.

Sample name	Glass composition (mol%)				
	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	HfO ₂
A	57.43	6.25	13.99	22.33	0
B	57.43	6.25	36.32	0	0
C	56.54	6.15	13.77	21.98	1.56

2.2.2 Optimized protocol definition for Hf-doped glasses

The influence of different experimental parameters (HfO_2 particle size, fusions number, melting time and temperature) has been checked for the C glass elaboration in order to optimize the process (Table 2). The powder mixture (≈ 3 g) was melted in a C-SiC crucible under Ar atmosphere. After melting, the molten glass was cooled by shutting off the heat source (cooling rate $< 8^\circ\text{C}/\text{min}$). In case of several meltings, each remelting was preceded by a glass sample milling step (WC vessel and ball, Mixer Mill MM 200) to ensure its homogenization. Final glass samples were removed from the crucible and have roughly a 20 mm diameter and 6 mm height (Figure 2). An optimized protocol was then defined for Hf solubility measurements. To minimize hafnium sedimentation and its heterogeneities, fine HfO_2 powders were used (15 μm particle size). Remeltings enabled to homogenize the whole glass melt. The 3h run duration allowed to avoid bubbles and longer run duration did not really impact the HfO_2 dissolution and had the drawback of increasing the Na volatilization. Thus, the experimental procedure followed for solubility measurements comprised three meltings for 3h at 1250°C or 1400°C with two intermediate glass millings (Figure 1).

Table 2

Glass elaboration parameters of 1.56 mol% HfO_2 -doped glasses melted in C-SiC crucible.

Sample name	Glass elaboration parameters			
	Melting time	Melting temperature	HfO_2 particle size	Fusions number
C0	3h	1250°C	70 μm	1
C1	12h	1250°C	70 μm	1
C2	3h	1400°C	70 μm	1
C3	3h	1250°C	158 μm	1
C4	3h	1250°C	15 μm	1
C5	3h + 3h	1250°C	70 μm	2
C6	3h + 3h + 1h	1250°C	70 μm	3

A and B glass powders were respectively mixed with different amounts of HfO_2 , ranging from 1.56 mol% to 10 mol% HfO_2 in the final glass. The powder mixture was fused either in a Pt-Au crucible and air atmosphere (oxidizing conditions) or in a C-SiC (or C_g) crucible under Ar atmosphere (reducing conditions). Glasses were directly quenched in air (cooling rate about $100^\circ\text{C}/\text{min}$) and then milled. The milling and remelting steps were done twice. Finally, the crucible was removed from the hot furnace and quenched immediately by immersing the bottom of the crucible into a cold water bath to prevent crystallization during cooling (cooling rate about $100^\circ\text{C}/\text{s}$). Glasses were not annealed.

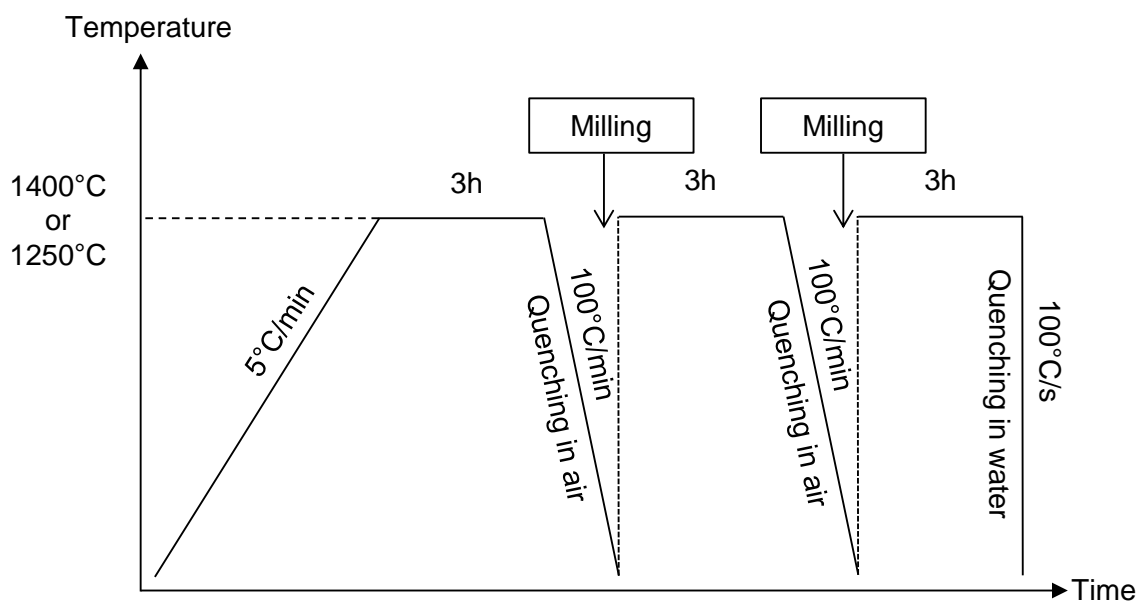


Figure 1. The general procedure of glass elaboration for Hf solubility measurements.

2.3 Glass characterizations

2.3.1 Homogeneity

Glass sample homogeneity was determined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Secondary phases morphology and size were observed by SEM (Phillips XL30-WTMP and ZEISS Supra 55 FEG) coupled with energy dispersive X-ray spectroscopy (Brucker EDS analyser) allowing glass composition semi-quantitative analysis. The conditions for electron microprobe analysis were an acceleration voltage 15 keV, a total of $5 \cdot 10^5$ counts and a Phirho(Z) method with standards. For SEM observations, crucible-shaped glass samples were cut in the middle and mounted in epoxy resin before being polished and carbon coated. Crystalline phases were identified by a PANalytical diffractometer (X'Pert MPD Pro, Bragg-Bretano geometry using a Ni-filtered the Cu K α radiation, solid detector X'Celerator) using the EVA software from Bruker AXS company. The data acquisition was completed in the step scan mode (10-90° 2 θ , step size 0,017° 2 θ , total time counting of at least 5h). XRD measurements were carried out on glass powders. The modelization of the X-ray pattern was performed in two steps using the Fullprof_Suite program [21]. Lattice parameters were first determined by the whole pattern decomposition then the structure was modeled by the Rietveld technique. Rietveld refinement was realized for highly crystallized glasses to assess the phases inventory previously done and obtain the relative mass fraction of each crystalline phase. For the latter, the amorphous phase is not considered.

2.3.2 Properties

The glass density was measured using a hydrostatic balance; the glass was weighed in air and then, in water according to Archimedes' principle. The reported density represents the mean value of three measurements.

Viscosity measurements were performed by a stress imposed rheometer (Rheometrics Scientific SR 5000) [22]. Basically, the rheometer was located above a vertical tubular furnace and a cylindrical crucible was placed in the furnace center. Rheological measurements were realized with a cylindrical rotor in the Couette geometry. Measurements

were performed at several temperatures. For Newtonian melts, a model following a Vogel-Fulcher-Tammann (VFT) law was applied [23].

3 Results

3.1 Hafnium incorporation

3.1.1 Sedimentation and heterogeneities

The C3 glass sample containing 1.56 mol% HfO_2 (158 μm particle size) and elaborated for 3 hours at 1250°C is firstly observed. The glass is transparent with a slightly yellowish tint, probably, due to minor contamination from the crucible or the grinding vessel (Figure 2) [8]. Hafnia sedimentation is clearly observed at the bottom (Figure 2a) and the sample displays two distinct parts. In the top half, glass seems to be homogeneous without any crystalline phases, which is confirmed by SEM images (Figure 2b). Few bubbles are noticed. Heterogeneities, composed of crystal clusters, are only detected at the bottom (Figure 2b). According to XRD patterns, the crystalline phases are monoclinic HfO_2 , hexagonal $\text{Na}_4\text{Hf}_2(\text{SiO}_4)_3$ and triclinic $\text{Na}_2\text{ZrSi}_2\text{O}_7$ (more details in paragraph 3.2.2). Graphite C_g is also detected by XRD. Hafnium being a heavy element, it is easily observable using back scattered electrons (BSE). In the analyzed section, $\text{Na}_4\text{Hf}_2(\text{SiO}_4)_3$ and HfO_2 crystals are identified by SEM (Figure 2c) contrary to the crystalline phase $\text{Na}_2\text{ZrSi}_2\text{O}_7$. White halos surrounding these crystals are also observed in BSE (Figure 2b), which demonstrates hafnium enrichment in the vitreous matrix. An hafnium concentration gradient in the glass matrix is observed in the whole sample, a lower concentration at the top and in the middle of sample (between 0.3 and 0.4 mol% HfO_2) than at the bottom (1.3 mol% HfO_2) (Figure 3a).

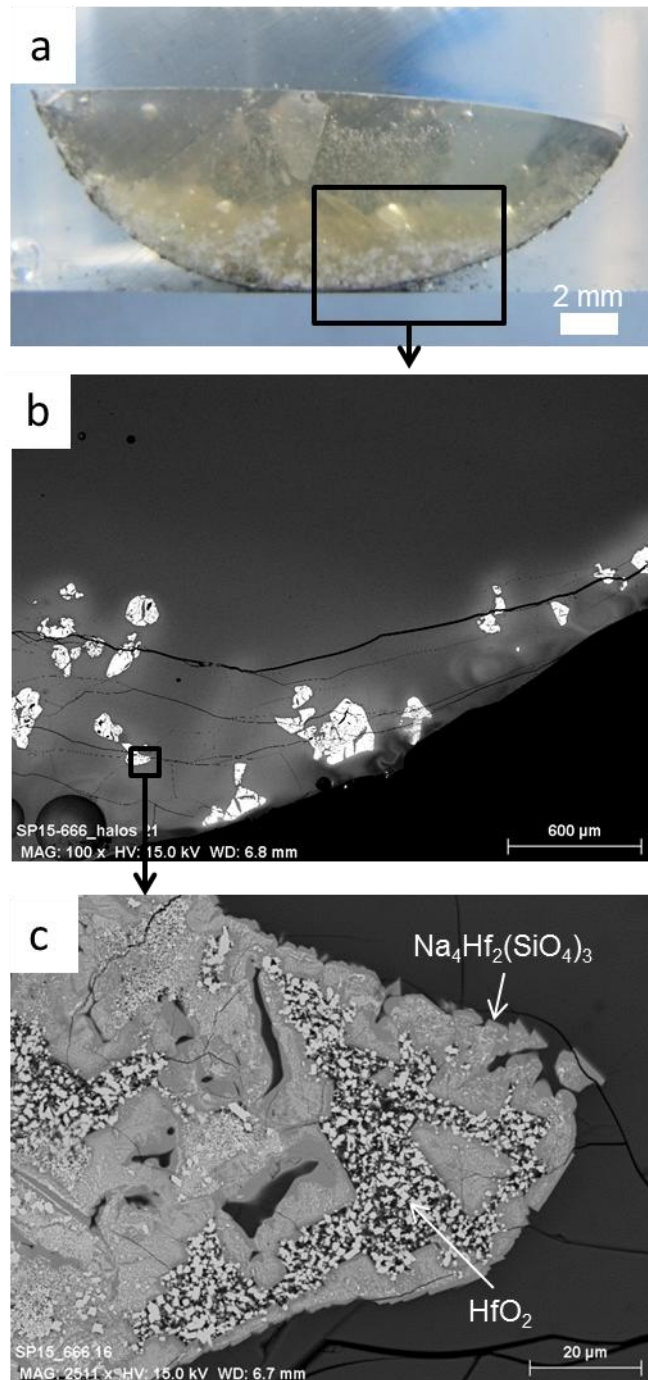


Figure 2. Picture (a) and scanning electron microscopy images (b) and (c) of heterogeneities observed in Hf-doped glass (C3 sample).

To avoid these heterogeneities, several parameters were investigated such as hafnium precursor particle size, run duration, meltings number and temperature (Table 1). The glass sample microstructure was observed by SEM (Figure 4) and the HfO_2 concentration in glass network was determined by EDS analysis in three specific glass areas and compared to the targeted value, 1.56 mol% HfO_2 (Figure 3). The absence of HfO_2 compositional gradients in the glass was one of the features consistent with an approach to equilibrium.

3.1.2 Effect of precursor particle size

C0, C3 and C4 glass samples followed identical thermal treatment (1250°C, 3h) but were prepared with different hafnium powder particle sizes, namely and respectively 158, 70 and 15 μm . The decrease of the HfO_2 particle size widely limits the HfO_2 sedimentation by decreasing the amount and size of hafnium crystals in the glass (Figure 4a, b and c). The size of agglomerated crystals is from 200 to 400 μm sized in the C3 glass compared to 50-100 μm in the C0 glass. In the C4 glass, where hafnium particle size is very fine (15 μm), only a few of those crystals are noticed. Moreover, reactivity between glass and hafnium powders is enhanced using fine powders (increase of the reactive surface for a given volume). As a consequence, hafnium concentration in the glass melt is largely increased and almost reaches the targeted value (Figure 3a). However, a concentration gradient still remains in the whole sample. In the next parts, the intermediate 70 μm particle size (C0 glass) is selected to study the effect of the other parameters.

3.1.3 Effect of melting time

C0 and C1 glasses were elaborated at 1250°C for, respectively 3h and 12h. Increasing melting time does not change the samples general feature. White halos, hafnium concentration gradient and hafnium crystals at the bottom were still identified in the C1 glass (Figure 3b and Figure 4d). Nevertheless, hafnium concentration is higher at the bottom and the middle in the C1 glass than in the C0 one (about 40-50% more). On top of the sample, the hafnium concentration remains the same.

3.1.4 Effect of remelting

To achieve good homogenization, glasses are usually milled and melted several times [9, 11, 20]. A standard remelting procedure was introduced with an intermediate milling step. Glass samples were melted once (C0 glass), twice (C5 glass) or three times (C6 glass) at 1250°C (Table 2). The hafnium concentration gradient has almost vanished after the second melting (Figure 3c). Hafnium concentration in the C5 glass is very close to the targeted value. Nevertheless, few hafnium crystals still stay at the bottom. After the third melting, C6 glass is homogeneous in concentration and only one hafnium crystal is found in the whole sample (Figure 4f). Bubbles are observed in both C5 and C6 glasses because of introduced air by the milling step. The milling step appears to be essential to homogenize the glass. This method (successive milling and remelting steps) is a convenient way of “stirring” the melt, and thus of improving dissolution kinetics, when thermal treatments can only be realized under static conditions [6, 24].

3.1.5 Effect of melting temperature

The impact of the melting temperature was briefly studied. Indeed, some authors managed to get equilibrated melts by increasing the temperature up to 1560°C [8]. In this study, the melting temperature was limited to 1400°C to minimize Na volatilization. A C2 glass sample was synthesized at 1400°C for 3h. Figure 3d shows that temperature increasing improves hafnium solubilization in the whole glass. Nonetheless, hafnium concentration gradient is also emphasized. At the bottom, a thick and whiter Hf-rich layer, about 0.65-1 mm (versus the 6 mm glass height) is observed (Figure 4e). This layer contains HfO_2 crystals and the surrounding Hf concentration is estimated up to 7.5 %mol HfO_2 in the melt. Above that layer, the Hf concentration is below 1.56 mol%. The crystalline phase $\text{Na}_4\text{Hf}_2(\text{SiO}_4)_3$ seems to be entirely dissolved in the glass at 1400°C as a reaction intermediate.

As expected, the C-SiC crucible provides a strong reducing environment and is able to reduce part of Na_2O to the metallic form Na^0 at high temperature [25]. In these experiments,

the glass lost, respectively, 14% and 28% of Na_2O after 3h and 12h at 1250°C. The Na loss was around 37% after two meltings of 3h at 1250°C and 38% after 3h at 1400°C. These first experiments enabled to define an optimized Hf-doped glass elaboration procedure (Figure 1) allowing to approach the equilibrium and thus to measure solubility limits, while limiting the compositional changes due to alkali loss.

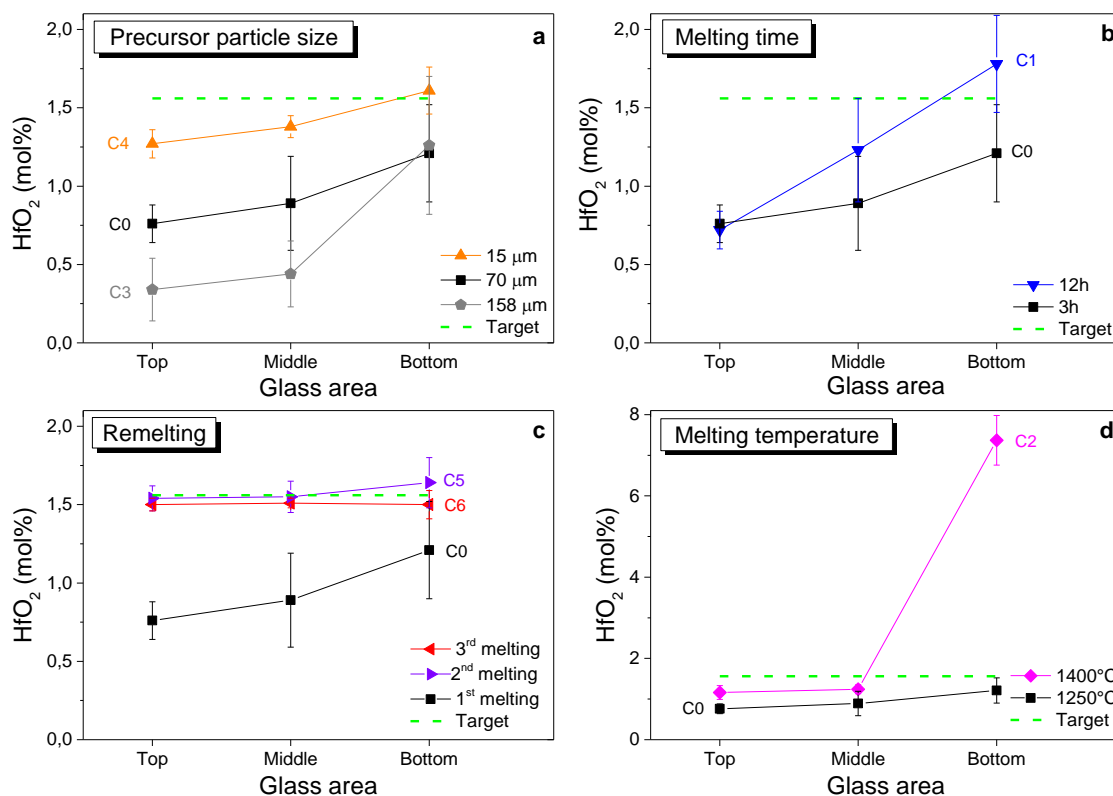


Figure 3. Variation in HfO_2 concentration as a function of glass area for several glasses elaborated in different conditions. Impact of (a) HfO_2 particle size, (b) melting time, (c) remelting, (d) melting temperature. HfO_2 concentration as related to mole percent. Error bars represent the random standard uncertainty calculated by multiplying the standard deviation of the mean and the student t-factor at the 95% level of confidence.

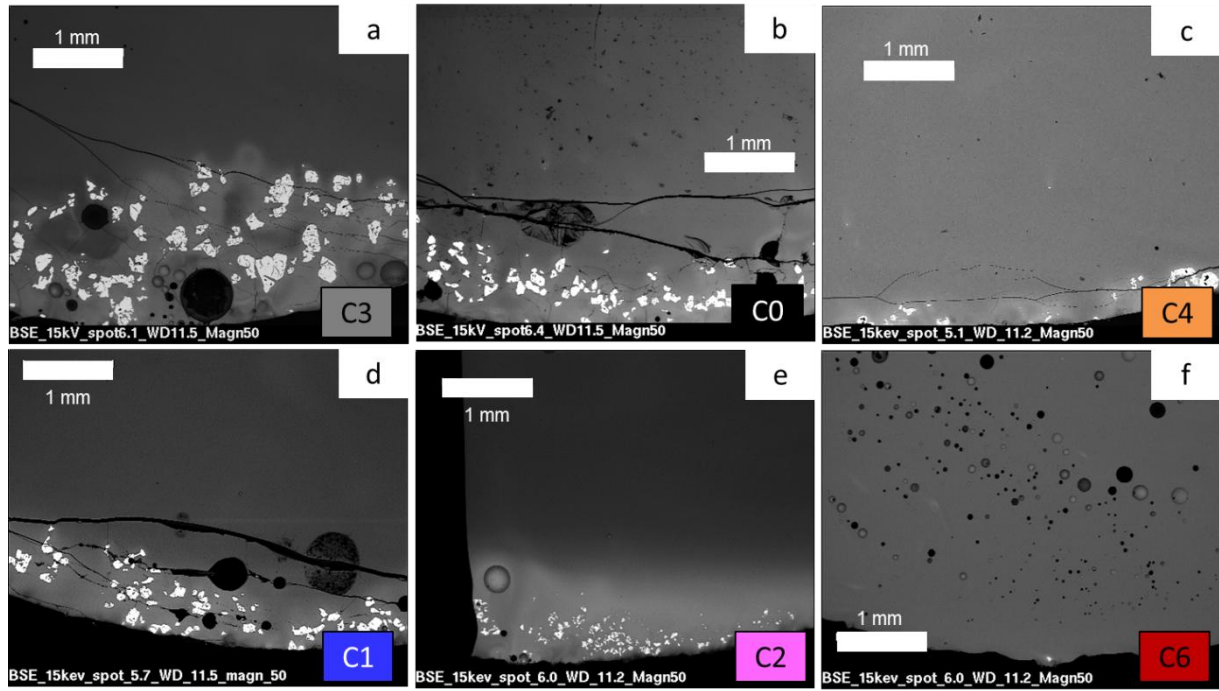


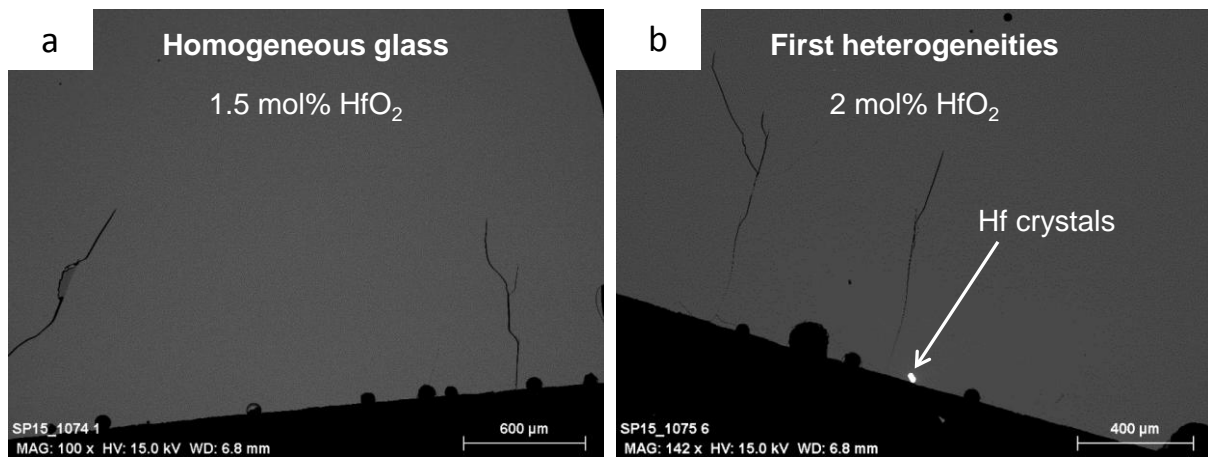
Figure 4. SEM images of Hf-doped glasses melted in different conditions: effect of (a,b,c) particle size, (b,d) melting time, (b,e) melting temperature, and (b,f) remelting. The name of observed glasses is given at the bottom right corner.

3.2 Solubility study

3.2.1 Hafnium solubility

The HfO_2 solubility in the aluminosilicate glass was determined in oxidizing (Pt-Au crucible) and reducing (C-SiC or C_g crucibles) conditions at 1250°C and 1400°C for A glasses and only at 1400°C for B glasses, because below 1327°C , B melt starts to crystallize. Both conditional (S_C) and saturation (S_S) solubilities were measured and are indicated in Table 3. The S_C is determined by progressively increasing the amount of added HfO_2 in the glass until the formation of Hf-bearing crystals (Figure 5a and b). The lower limit corresponds to the maximal quantity of Hf that could be incorporated in the homogeneous glass matrix. And the upper limit refers to the quantity of Hf where the first heterogeneities are observed. The S_S is characterized by HfO_2 concentration measurements in a HfO_2 -saturated glass with Hf-bearing crystals (Figure 5c and d). The main glasses compositions are shown in Table 4. Each Hf concentration value represents an average of several measurements (from 6 to 12 points of EDS analyses).

Gradation



Saturation

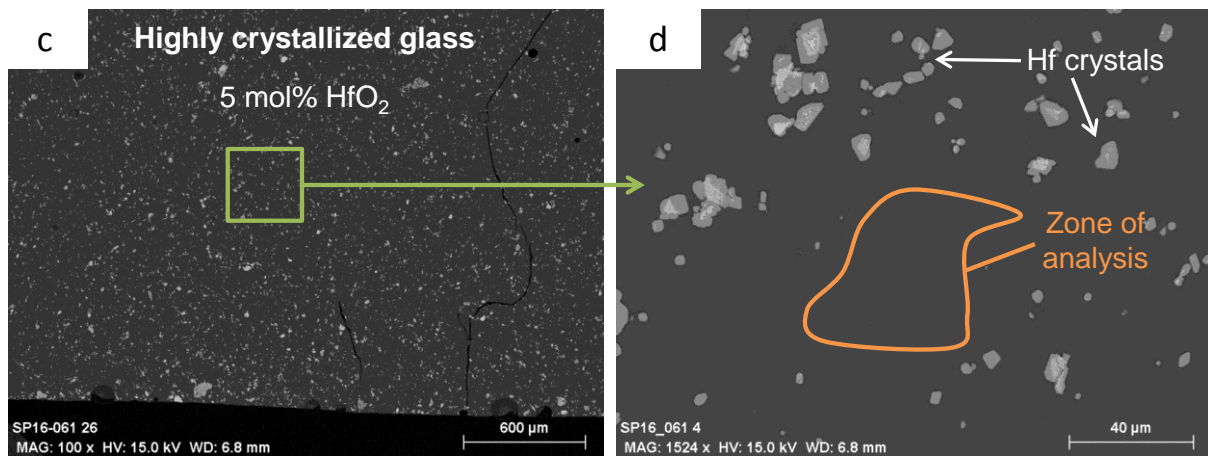


Figure 5. SEM images of Hf-doped A glasses, elaborated in Pt-Au crucible at 1250°C, containing (a) 1.5 mol%, (b) 2 mol% and (c,d) 5 mol% HfO₂, showing the two methods for the solubility measurements (gradation and saturation).

Table 3

Solubility limits of hafnium determined in A and B aluminosilicate glasses elaborated in oxidizing and reducing conditions at 1250°C and 1400°C.

conditions at 1250 °C and 1400 °C.					
Hf-doped glasses	Melting conditions			Hafnium solubility limits	
Glass series	T (°C)	Crucible	Atmosphere	Conditional solubility (HfO ₂ mol%)	Saturation solubility (HfO ₂ mol%)
A-series	1250	Pt-Au	Air	$1.5^a < S_c < 2^c$	3
	1250	C-SiC	Air - Ar	$2.5^a < S_c < 3^c$	/
	1400	Pt-Au	Air	$5^a < S_c < 7^c$	6 - 6.5
	1400	C-SiC	Air - Ar	$3^b < S_c < 5^c$	4.5
B-series	1400	Pt-Au	Air	$3^a < S_c < 4^c$	5.5- 6
	1400	C-SiC	Air - Ar	$3.5^a < S_c < 4^c$	3.5 - 4
	1400	C _g	Air-Ar	/	6

^a Homogeneous glass

^b Glass containing dendritic crystals

^c Glass containing crystals

The measured conditional solubility is either lower or close to the saturation solubility. The S_s limit is higher than the upper S_c limit only for two Hf-bearing glasses: A and B glasses melted in a Pt-Au crucible at 1250°C and 1400°C respectively. This suggests that the glass elaboration conditions were well-optimized to reach equilibrium for most glasses. However, the saturation solubility is independent of hafnium dissolution kinetics contrary to the conditional solubility. In the nuclear field, the conditional solubility has been used to compare actinides and surrogates [10, 12]. This solubility ensures that the glass sample is totally homogeneous for a given glass-making protocol but does not necessarily correspond to the maximum amount that can be incorporated in the glass. In the following, we will essentially consider the saturation solubility. Indeed, we can consider that saturation experiments provide us hafnium concentrations close to the equilibrium concentration, as no hafnium concentration gradient is observed. Only the A glass with 10 mol% HfO₂ melted in C-SiC crucible at 1250°C (AS8 sample) showed a concentration gradient, and consequently, the HfO₂ saturation solubility limit was not determined for it. Furthermore, an excess of hafnium above the saturation solubility should not significantly change the saturation concentration of HfO₂.

The redox conditions (oxidizing or reducing conditions) do not affect the hafnium solubility. Saturation experiments in C_g and Pt-Au crucibles for the B-series show that BS4 and BS5 glasses exhibit the same saturation concentration about 5.5-6 mol% HfO₂ at 1400°C.

The hafnium concentration of HfO₂-saturated melts increases with the melting temperature, from 3 mol% HfO₂ at 1250°C to 6-6.5 mol% HfO₂ at 1400°C for the As-series melted in a Pt-Au crucible.

The hafnium solubility also depends on the glass composition. At 1400°C in oxidizing conditions, the Bs-serie glasses exhibit a solubility of 5.5-6 mol% and the As-series, a slightly higher of 6-6.5 mol% HfO₂. Furthermore, glasses melted in C-SiC crucibles (AS7 and BS2 glasses) exhibit lower solubilities than glasses elaborated in Pt-Au or C_g crucibles (AS5, BS4 and BS5 glasses): 4.5 mol% HfO₂ for A melts and 3.5-4 mol% HfO₂ for B melts. This can be explained by the use of C-SiC crucible that interacts with the glasses and modifies their compositions. Indeed, at high temperature, the mullite binder (3Al₂O₃-2SiO₂) diffuses in the glass as proven by the enrichment of Al₂O₃ and SiO₂ in AS7 and BS2 samples (Table 4).

Table 4

Glass compositions (mol%) determined by microprobe (EDS) and crystalline phases observed for different elaboration conditions. The M* ratio is expressed as molar (CaO+Na₂O)/(CaO+Na₂O+Al₂O₃) ratio. The random standard uncertainty is calculated by multiplying the standard deviation of the mean and the student t-factor at the 95% level of confidence.

Glass Name	Starting glass	Temperature (°C)	Redox conditions	Added HfO ₂ (mol%)	SiO ₂ (mol%)	Al ₂ O ₃ (mol%)	CaO (mol%)	Na ₂ O (mol%)	HfO ₂ (mol%)	Fe ₂ O ₃ (mol%)	Crystalline phases	M*
AS1	A	1250	Pt-Au	1.5	57.30 +/- 0.10	6.30 +/- 0.03	13.91 +/- 0.05	20.82 +/- 0.08	1.66 +/- 0.05	0	None	0.85
AS2	A	1250	Pt-Au	4.0	57.54 +/- 0.30	6.34 +/- 0.07	13.78 +/- 0.09	19.25 +/- 0.24	3.09 +/- 0.08	0	Na ₄ Hf ₂ (SiO ₄) ₃ , HfO ₂	0.84
AS3	A	1250	C-SiC	2.5	62.44 +/- 0.49	7.72 +/- 0.12	13.41 +/- 0.49	13.90 +/- 0.39	2.53 +/- 0.07	0.31 +/- 0.03	None	0.78
AS4	A	1400	Pt-Au	5.0	55.60 +/- 0.12	6.02 +/- 0.04	13.20 +/- 0.06	20.01 +/- 0.08	5.17 +/- 0.09	0	None	0.85
AS5	A	1400	Pt-Au	7.0	55.19 +/- 0.09	6.13 +/- 0.03	13.28 +/- 0.12	19.36 +/- 0.16	6.04 +/- 0.07	0	Na ₄ Hf ₂ (SiO ₄) ₃ , HfO ₂	0.84
AS6	A	1400	C-SiC	3.0	65.02 +/- 0.91	7.95 +/- 0.30	13.17 +/- 0.92	10.59 +/- 0.53	3.02 +/- 0.15	0.26 +/- 0.04	Dendrites	0.75
AS7	A	1400	C-SiC	7.0	65.77 +/- 0.17	8.60 +/- 0.09	11.98 +/- 0.46	8.93 +/- 0.17	4.52 +/- 0.08	0.21 +/- 0.17	HfO ₂	0.71
BS1	B	1400	C-SiC	3.5	61.16 +/- 0.24	7.50 +/- 0.05	28.27 +/- 0.22	0	3.07 +/- 0.07	0	None	0.79
BS2	B	1400	C-SiC	7.0	61.77 +/- 0.37	8.49 +/- 0.23	24.60 +/- 0.78	1.07 +/- 0.21	3.56 +/- 0.14	0.51 +/- 0.21	HfSiO ₄ , HfO ₂	0.75
BS3	B	1400	Pt-Au	3.0	56.65 +/- 0.07	6.23 +/- 0.02	34.11 +/- 0.11	0	3.02 +/- 0.06	0	None	0.85
BS4	B	1400	Pt-Au	7.0	54.92 +/- 0.05	6.55 +/- 0.03	32.91 +/- 0.09	0	5.61 +/- 0.06	0	Ca ₂ HfSi ₄ O ₁₂ , HfSiO ₄	0.83

											HfO ₂	
BS5	B	1400	C _g	7.0	55.00 +/- 0.11	6.12 +/- 0.03	32.89 +/- 0.11	0	5.99 +/- 0.05	0	HfSiO ₄ ⁴ , HfO ₂	0.84

3.2.2 Hafnium crystallization

The mineralogy of the different crystals-bearing glasses above the HfO₂ solubility limit changes with the glass composition and the redox conditions (Table 4). For the A-series glasses elaborated in oxidizing conditions (1250°C or 1400°C), the main crystallized phase is hexagonal Na₄Hf₂(SiO₃)₄ as shown in Figure 6 and Figure 7b. The Rietveld refinement attests that those crystals represent 79 wt% of the whole crystalline phases attended (Table 5). Monoclinic HfO₂ crystals (21 wt%) are also identified by both XRD and SEM/EDS.

In the A-series melted in C-SiC crucible at 1400°C, the only Hf-bearing crystallized phase is HfO₂. Some cristobalite (SiO₂) is also detected (around 30 wt%). At lower temperature, the other crystalline phase (40 wt%) seems to correspond to the triclinic parakeldyshite Na₂ZrSi₂O₇ phase [26]. Because of the possible cross-substitution of Zr and Hf, the formula of the observed crystalline phase in Figure 7a might correspond to Na₂HfSi₂O₇. This stoichiometry is confirmed by EDS analysis of the crystal (Table 6). Na migration under electron beam may explain the slight drop between the analysis and the pure phase stoichiometry. EDS analysis also suggests that a substitution of Na₂O by CaO is also likely to occur in that crystal. Since no XRD pattern of Na₂HfSi₂O₇ is referenced in the literature to our knowledge, we have first considered the same space group for Na₂Hf₂SiO₇ than for parakeldyshite. The atomic positions of parakeldyshite were used with a complete substitution of Zr by Hf. The Rietveld refinement of the XRD pattern is consistent with this result, as shown by the χ^2 equal to 4.9 (Figure 8). The cell parameters of the Na₂HfSi₂O₇ crystalline phase are extracted from the refinement and given in Table 7. In order to validate the refinement, the sodium hafnium disilicate Na₂HfSi₂O₇ was synthesized and its structure was refined. The triclinic space group was confirmed and the atomic positions were determined [27].

For the B-series glasses (Na-free) elaborated in oxidizing conditions, monoclinic Ca₂HfSi₄O₁₂, tetragonal HfSiO₄ and HfO₂ crystals are observed by SEM (Figure 7d) and detected by XRD (Figure 6). The main phase is Ca₂HfSi₄O₁₂ (89 wt%) and other phases are HfO₂ (6 wt%) and HfSiO₄ (5 wt%). In reducing conditions, the crystallized phases are HfSiO₄ and HfO₂ according to XRD results (Figure 6). For glasses melted in C-SiC crucibles, HfO₂ crystals are not detected by XRD (certainly below the device detection limit) but some tiny ones (few hundred of nanometers) are shown up in SEM images (Figure 7c). However, XRD patterns often show the presence of graphite carbon and silicon carbide. These impurities come from the reaction between glass and C-SiC crucible at the glass/crucible interface. A thin layer belonging to the C-SiC crucible was systematically observed on the sample surface after heating. So a variable part of this layer could be introduced in the sample during the XRD preparation. The C and SiC content are not taken into account in the crystalline phase percentage calculation.

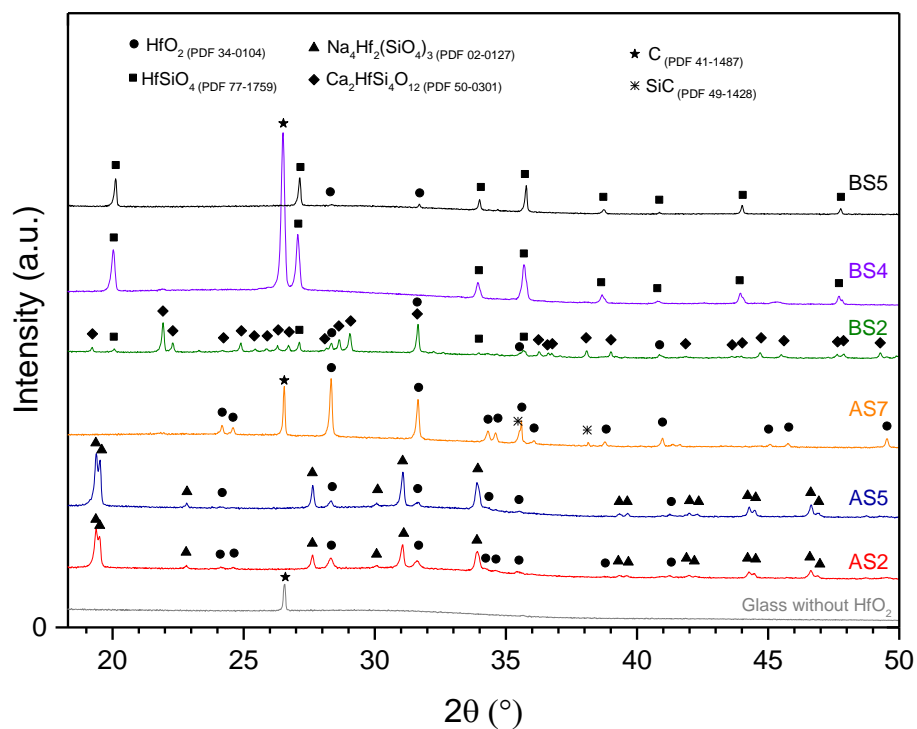


Figure 6. XRD patterns of Hf-doped glasses elaborated in oxidizing and reducing conditions at 1250°C or 1400°C. The glass sample without adding HfO₂ was melted in C-SiC crucible at 1400°C for 3h. Note that the enlarge part of patterns between $2\theta = 18-50^\circ$ is shown to get better insight of the diffraction peaks due to the crystallization.

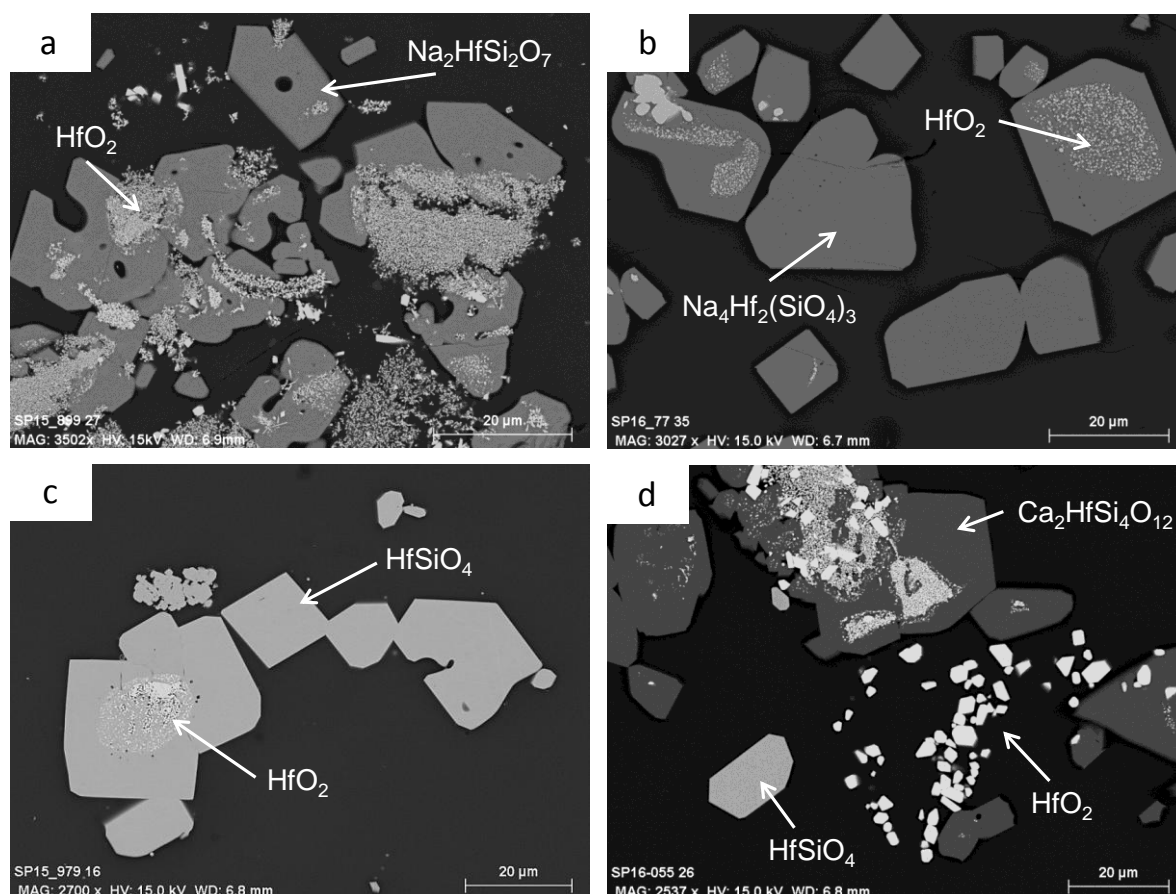


Figure 7. SEM images of crystals in HfO_2 -saturated glasses from A starting glass (a) at 1250°C in C-SiC crucible, (b) at 1250°C or 1400°C in Pt-Au crucible and from B starting glass at 1400°C (c) in C-SiC or C crucibles, (d) in Pt-Au crucible.

Table 5

Relative percentage in mass of some crystals in glass, data obtained after the Rietveld refinement of crystallized glass samples. Error for each crystal is ± 2 wt%.

Glass	Crystal mass fraction (wt%)						X^{2*}
	$\text{Ca}_2\text{HfSi}_4\text{O}_{12}$	$\text{Na}_4\text{Hf}_2\text{Si}_3\text{O}_{13}$	$\text{Na}_2\text{HfSi}_2\text{O}_7$	HfSiO_4	HfO_2	SiO_2	
AS2	-	79 %	-	-	21 %	-	3.5
AS5	-	93 %	-	-	7 %	-	4.2
AS8	-	-	40 %	-	60 %	-	4.9
AS7	-	-	-	-	70 %	30 %	2.5
BS4	89 %	-	-	5 %	6 %	-	5.2
BS2	-	-	-	100 %	-	-	6.4

* Reduced chi square is an indicator of the fit goodness as determined in [21].

Table 6

Composition of the observed $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystalline phase determined by microprobe (EDS) in the studied sample (AS8) and compared to the stoichiometric one.

Chemical elements	O (at%)	Si (at%)	Na (at%)	Hf (at%)	Ca (at%)
Theoretical formula of $\text{Na}_2\text{HfSi}_2\text{O}_7$	58.3	16.7	16.7	8.3	0
Measured composition of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystal	60.1	17.6	11.6	8.4	2.4

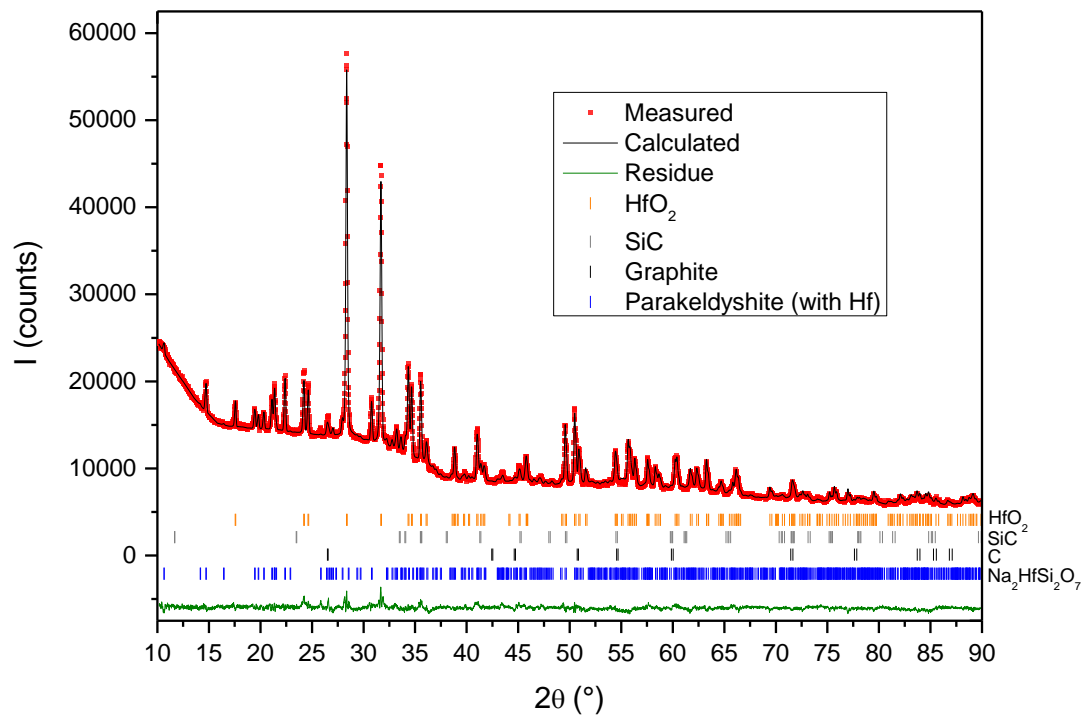


Figure 8. Rietveld refinement of XRD pattern containing the detected $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystalline phase in the A glass with 10 mol% HfO_2 melted in C-SiC at 1250°C (AS8).

Table 7

Cell parameters (a, b, c, α , β , γ and cell volumes) of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystals present in the studied sample, extracted from the whole pattern decomposition, and of the triclinic $\text{Na}_2\text{ZrSi}_2\text{O}_7$ crystals.

Crystalline phase	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	Ref
$\text{Na}_2\text{HfSi}_2\text{O}_7$	6.6232	8.7881	5.4046	92.25	93.88	71.10	296.89	This study
	+/-	+/-	+/-	+/-	+/-	+/-	+/-	
	0.0060	0.0075	0.0047	0.09	0.07	0.06	0.45	
$\text{Na}_2\text{ZrSi}_2\text{O}_7$	6.6364	8.8120	5.4233	92.69	94.20	71.36	299.6	[26]

Hf-bearing crystals display different forms (Figure 7). HfO_2 gets two types of crystal sizes, several hundred nanometers and several microns. Micrometric crystals are located in the glass and have an isometric shape while nanometric HfO_2 are often observed inside the Hf silicate crystals. These silicate crystals have an isometric shape and range in size from 10 μm to 50 μm . Other crystal morphologies are also observed in the A-series fused in C-SiC at 1400°C (Figure 9). These hafnium crystals are located at the interface between the glass and the crucible and display several forms such as needle (Figure 10a), dendrite (Figure 10b and c) and crown (Figure 10d) shapes. Surrounding these crystals, a depletion of HfO_2 and CaO and an enrichment of other oxides (SiO_2 and Al_2O_3) are noticed (Table 8). Those crystals are not observed using Pt-Au crucibles.

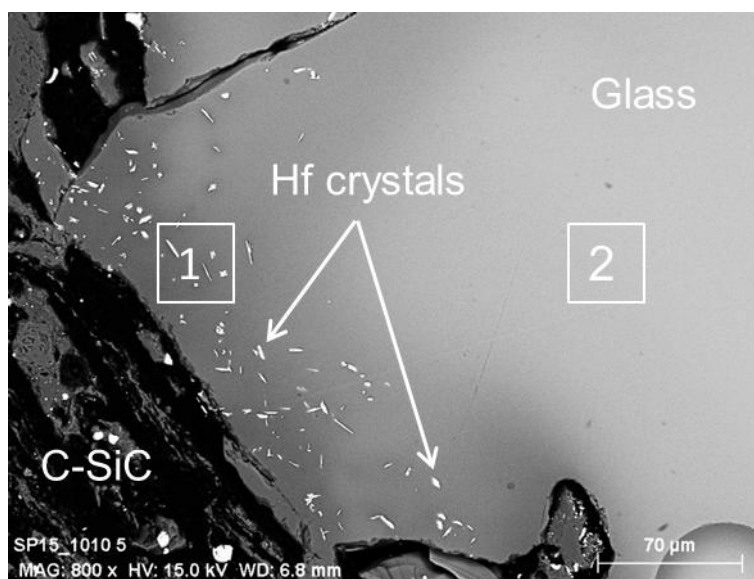


Figure 9. SEM image of the interface between the C-SiC crucible and the glass in the AS6 sample, showing (1) and (2) different areas.

Table 8

Glass compositions of two areas; (1) close to the interface between the C-SiC crucible and the glass and (2) far from this interface; determined by microprobe (EDS) in the AS6 sample.

Point of analysis	SiO ₂ (mol%)	Al ₂ O ₃ (mol%)	CaO (mol%)	Na ₂ O (mol%)	HfO ₂ (mol%)	Fe ₂ O ₃ (mol%)
1	77.63	9.44	2.71	7.81	2.30	0.11
2	67.85	8.42	10.75	8.39	4.31	0.29

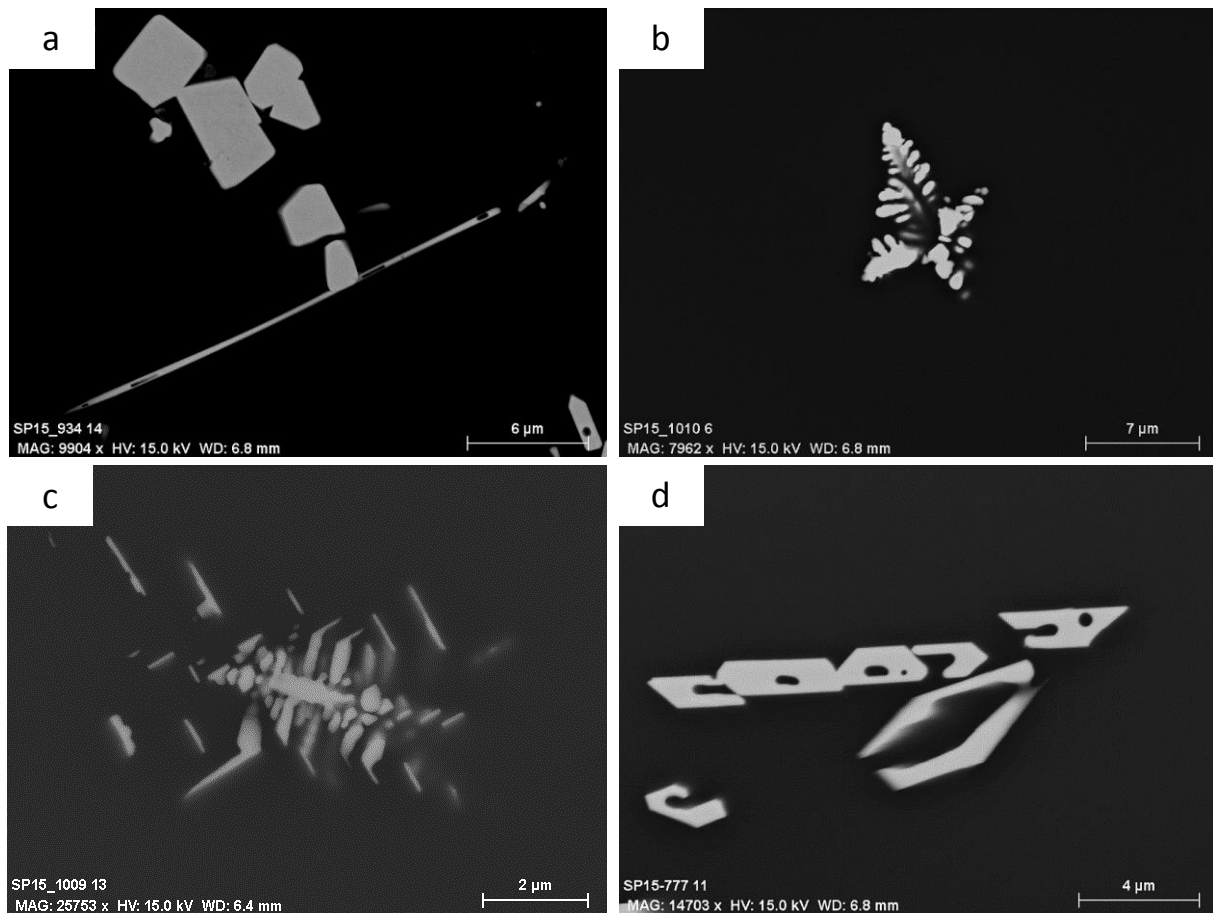


Figure 10. SEM images of Hf-bearing crystals observed in Hf-doped A glasses melted in C-SiC crucible at 1400°C with several morphologies (a) needle shaped, (b,c) dendritic shaped and (d) crown shaped .

4 Discussion

4.1 Hafnium incorporation

Hafnium sedimentation may be explained by the huge density difference between HfO₂ precursor and the glass. Measured glass densities are respectively, 2.59 g.cm⁻³ and 2.68 g.cm⁻³ for A and C glasses in contrast to 9.68 g.cm⁻³ for HfO₂. Experimental measurements indicate that A and C melt viscosities are below 200 dPa.s at 1250°C and close to 50 dPa.s at 1400°C (Figure 11). Hafnium addition in the glass network increases slightly the melt

viscosity but not enough to avoid HfO₂ sedimentation. In a laminar flow, the sedimentation velocity (m.s⁻¹) of spherical particles in a melt can be described by the Stokes' law:

$$v = \frac{2r^2 g(\rho_{particle} - \rho_{fluid})}{9\eta} \quad (1)$$

with r , the particle radius (m)
 g , the standard acceleration (m.s⁻²)
 ρ , the density (kg.cm⁻³)
 η , the fluid viscosity (Pa.s)

Considering these hypotheses (laminar flow and spherical particles) and equation (1), 158 μ m diameter HfO₂ particles in A melt fall in about 15 min from the top to the bottom of the glass sample (around 6 mm) at 1250°C and more rapidly in 5 min at 1400°C. HfO₂ sedimentation is accelerated at 1400°C, while hafnium diffusion into the glass melt is enhanced. Equation (1) also shows that decreasing HfO₂ particle size drastically slows down the sedimentation velocity. At 1250°C, 70 μ m diameter HfO₂ particles fall in 75 min and 15 μ m diameter HfO₂ particles in more than one day. This effect has to be coupled with the increase in Hf precursors dissolution kinetics for smaller initial particle sizes [28], both leading to a better HfO₂ incorporation.

When equilibrium is not established, HfO₂ sedimentation widely limits its incorporation into the glass matrix. At the bottom of the crucible, the glass melt surrounding crystals is supersaturated in hafnium which largely slows down HfO₂ crystals dissolution into the whole glass sample. Furthermore, increasing duration could make the sedimentation layer denser [6] and thus makes it harder to dissolve crystals. In that case, crystallization is due to the presence of undissolved particles, relicts of hafnium oxide particles introduced into the initial powder mixture or to new formed crystals.

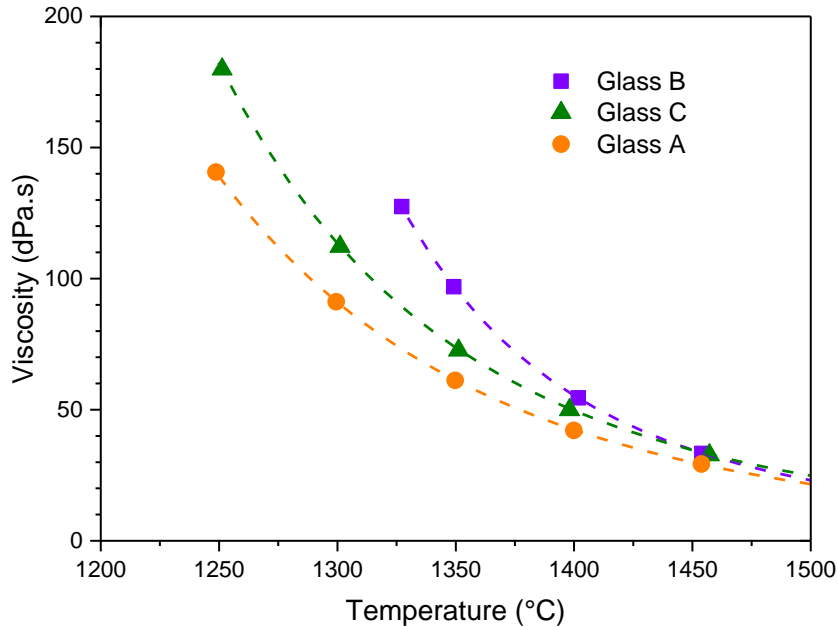


Figure 11. Steady state viscosity of glass melts for different compositions as a function of the temperature. The dash lines represent the VFT model and the symbols are the measured data. Note that all glasses are totally homogeneous within the measuring range.

4.2 Hafnium solubility

Our hafnium solubility results may now be compared to other studies. In this work, we show that the redox conditions do not affect the HfO_2 solubility which is consistent with the fact that Hf displays only one oxidation state in the glass, namely Hf^{IV} . Therefore the HfO_2 solubilization mechanism must be the same for reduced or oxidized glass melts.

A higher melting temperature improves the HfO_2 solubility limits as commonly observed by authors [10, 20, 24]. Since the oxidation state is fixed (Hf^{IV}), the enhancing of the solubility is only controlled by the temperature.

The interpretation of the HfO_2 solubility in aluminosilicate glass as a function of the glass composition is based on previous studies. For peralkaline glass, Davis [8] has demonstrated that the hafnium solubility is strongly and positively related to the excess of alkalis which are not used for charge compensation. We can define the following M^* ratio (with the oxide content in mol%):

$$M^* = \frac{M'O + M''_2O}{M'O + M''_2O + Al_2O_3} \quad (2)$$

where M' and M'' are respectively metal divalent and monovalent cations. According to Davis, for peralkaline glasses ($M^* \geq 0.5$), the hafnium solubility increases with M^* . Applied to our case M^* is written:

$$M^* = \frac{CaO + Na_2O}{CaO + Na_2O + Al_2O_3} \quad (3)$$

All our glass samples have $M^* > 0.5$ (Table 4) and belong to the peralkaline field. Glass samples melted in C-SiC crucibles present a lower M^* (0.71 and 0.74 for AS7 and BS2 samples) than glasses fused in other crucibles (0.84 and 0.83 for AS5, BS4 and BS5 samples). For AS7 glass sample, the lessening of M^* is accentuated by Na volatilization. A decrease in HfO_2 solubility is observed as M^* decreases (Table 3). Indeed, for AS7 and BS2 glasses, the melt compositions are enriched in Al_2O_3 and SiO_2 because of the mullite binder from the crucible, hence show a lower excess of alkalis or alkaline earths. Nevertheless, a slight solubility difference is observed between AS5 and BS4 glasses although their respective M^* are comparable. Therefore, it seems that the nature of cations may play a small role. Some authors [14, 15] have shown that, in peralkaline melts, the increase of the $M'O/M''_2O$ ratio smoothly enhances the solubilities of +4 cations (for instance, Ti and Zr). Thus, the substitution of Na_2O by CaO should slightly decrease the hafnium solubility as observed. When M^* is higher than 0.5, these cations act both as network modifiers and charge compensators in the aluminosilicate network. Classically, Ca^{2+} serves as a charge balancing for two AlO_4 tetrahedrons or two non-bridging oxygens and Na^+ charge balancing for one AlO_4 tetrahedron or one non-bridging oxygen. Ca might cause a steric hindrance more significant than Na. This assumption to explain the low HfO_2 solubility difference between AS5 and BS4 melts needs further experiments to confirm it.

Figure 12 presents our results compared to previous studies, with the HfO_2 solubility plotted as a function of the M^* ratio. The HfO_2 solubility is higher in peralkaline glasses than in peraluminous ones and borosilicate glasses tend to exhibit higher hafnium solubilities than aluminosilicate glasses. For the borosilicate glasses, the melting temperature is 50°C higher than in aluminosilicate glasses. Boron appears to improve the HfO_2 solubility but its role still remains unclear [8].

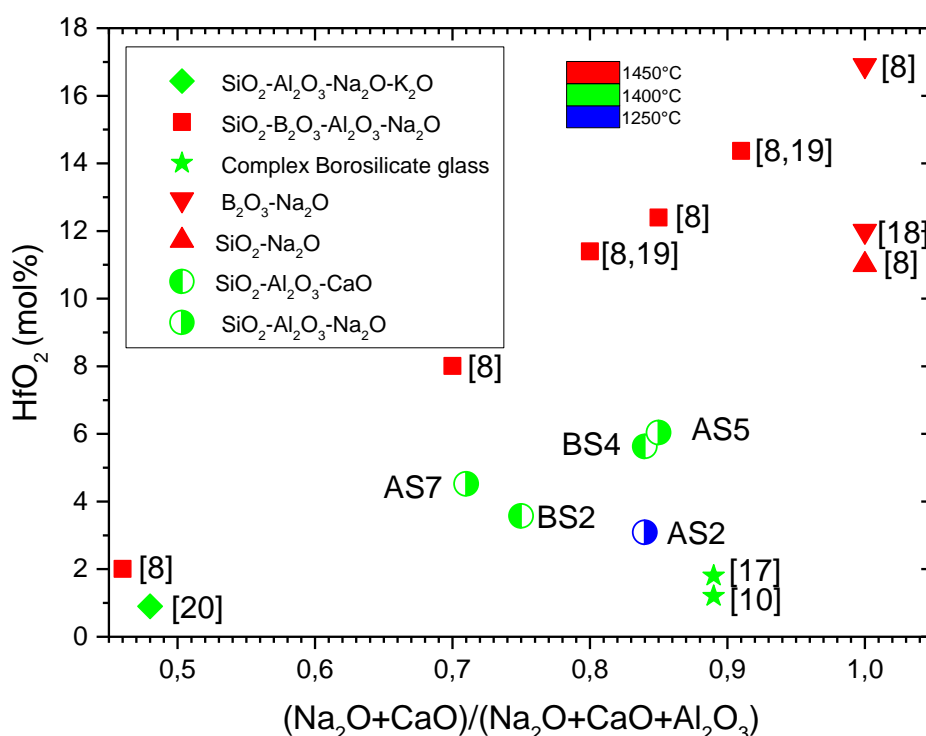


Figure 12. Comparison of hafnium solubility in A and B glasses to hafnium solubility in several types of glasses from the literature. HfO_2 concentration in mole percent is plotted as the function of the M^* ratio $(\text{CaO}+\text{Na}_2\text{O})/(\text{CaO}+\text{Na}_2\text{O}+\text{Al}_2\text{O}_3)$ in molar content.

4.3 Hafnium crystallization

The morphology of hafnium silicate crystals suggests that these crystals are quickly formed and quite stable in the melt. The HfO_2 crystals seem to grow following an Oswald ripening process [29, 30]. Nanometric HfO_2 are not observed in the melt but as inclusions in the hafnium silicate crystals indicating that they might have been poikilitically enclosed in the silicates before their growth.

Dendritic or needle crystals could be quench crystals [31]. As the temperature decreases during quenching, the glass melt becomes supersaturated with hafnium leading to a quick overgrowth of hafnium crystal along one or two preferential axes. However, those crystals are concentrated at the glass/crucible interface which is not logical for quench crystals. These crystals should also be observed in the core of the glass sample where the cooling rate is ordinarily the lowest. Moreover, the crown-shaped crystals do not really look like quench crystals. All this suggests that these crystals result from a reaction between the glass and the C-SiC crucible. The mullite binder might react with the glass melt in this area as shown by the glass enrichment in Al_2O_3 and SiO_2 and depletion in other elements (CaO and HfO_2). All these crystallization mechanisms are not fully understood in this work and need to be deepened.

The $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystalline phase has been detected for the first time. The existence of this phase is confirmed by its synthesis and its crystal structure determination. The Rietveld refinement of the XRD pattern containing this crystalline phase allows us to quantify it. The isomorphic character between the $\text{Na}_2\text{HfSi}_2\text{O}_7$ and the parakeldyshite $\text{Na}_2\text{ZrSi}_2\text{O}_7$ can be explained by close ionic radii for Hf and Zr for the same coordination number [32]. All detail

about the structure of $\text{Na}_2\text{HfSi}_2\text{O}_7$ are currently submitted and reviewed for a formal data deposition into XRD databases.

5 Conclusion

In this study, an experimental protocol has been developed in order to measure the hafnium solubility in aluminosilicate glass melted in both oxidizing and reducing conditions. Hf-doped glass elaboration conditions have been optimized to limit the HfO_2 sedimentation and to approach equilibrium. Contrary to the conditional solubility, the saturation solubility readily allows to determine a thermodynamic solubility. As hafnium speciation remains the same in the glass matrix (Hf^{IV}), its solubility is not affected by the redox conditions. In peralkaline glasses (with molar content $(\text{Na}_2\text{O}+\text{CaO}) > \text{Al}_2\text{O}_3$), the HfO_2 solubility limit is positively correlated with the melting temperature and the excess of network modifier cation (Na_2O and CaO) relatively to Al_2O_3 . The hafnium solubility also seems to be slightly impacted by the nature of these cations. These results are in agreement with previous studies of +4 cations in borosilicate or aluminosilicate glasses. The hafnium solubility appears to be higher in borosilicate glasses than in aluminosilicate glasses for a similar excess of alkalis or alkaline earths.

Above the hafnium solubility limit, formations of HfO_2 , HfSiO_4 , $\text{Ca}_2\text{HfSi}_4\text{O}_{12}$, $\text{Na}_4\text{Hf}_2(\text{SiO}_4)_3$ and $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystals have been observed in those glasses. The glass composition and potentially the redox conditions change the nature of the Hf-bearing crystals. The existence of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ crystalline phase has been evidenced in Na-rich aluminosilicate melts and for temperatures close to 1250°C . The Rietveld refinement of $\text{Na}_2\text{HfSi}_2\text{O}_7$ has been successfully performed. The $\text{Na}_2\text{HfSi}_2\text{O}_7$ phase structure appears to be very similar than the parakeldyshite $\text{Na}_2\text{ZrSi}_2\text{O}_7$ phase structure.

The optimization of Hf-doped glass elaboration conditions will be further used for the preparation of U-doped glasses. Indeed, the uranium incorporation in the glass melt faces to the same sedimentation issues [6]. Besides, UO_2 solubility is also likely to be related to the excess of alkalis [4]. The uranium behavior however remains more complex than the hafnium one. The chemistry of uranium in glass melt is ruled by the equilibria of $\text{U}^{\text{VI}}\text{-U}^{\text{V}}\text{-U}^{\text{IV}}$ [7]. The UO_2 solubility in glass melt as the function of the oxygen fugacity ($f\text{O}_2$) is the subject of ongoing studies and those data will be compared to the HfO_2 solubility.

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