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Solubility of actinide surrogates in nuclear glasses

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Abstract

This paper discusses the results of a study of actinide surrogates in a nuclear borosilicate glass to understand the effect of processing conditions (temperature and oxidizing versus reducing conditions) on the solubility limits of these elements. The incorporation of cerium oxide, hafnium oxide, and neodymium oxide in this borosilicate glass was investigated. Cerium is a possible surrogate for tetravalent and trivalent actinides, hafnium for tetravalent actinides, and neodymium for trivalent actinides. The material homogeneity was studied by optical, scanning electron microscopy. Cerium L_{III} XANES spectroscopy showed that the Ce^{3+}/Ce_{total} ratio increased from about 0.5 to 0.9 as the processing temperature increased from 1100 to 1400 °C. Cerium L_{III} XANES spectroscopy also confirmed that the increased Ce solubility in glasses melted under reducing conditions was due to complete reduction of all the cerium in the glass. The most significant results pointed out in the current study are that the solubility limits of the actinide surrogates increases with the processing temperature and that Ce^{3+} is shown to be more soluble than Ce^{4+} in this borosilicate glass.

1. Introduction

The minor actinide streams in reprocessing plants are currently planned to be incorporated in borosilicate glass matrices. The resulting glass must be fully homogeneous, i.e., all the constituent elements must be uniformly distributed in the glass matrix down to an atomic scale. The work discussed here is part of a study of actinide solubility in borosilicate glasses, undertaken to assess the extent of actinide solubility in these glasses, to understand the mechanisms controlling actinide solubilization, and to determine the structural role of actinides in these glasses. Glass specimens containing actinide surrogates are used to prepare and optimize the making of radioactive glass samples. It is therefore indispensable to identify the elements that best simulate the solubilization properties of the actinides. The choice is based on three criteria: the possible valence of the candidate elements, the ionic radii for a given coordination number, and the electronic configuration. This approach led us to select hafnium (Hf) and neodymium (Nd) as potential surrogates for the tetravalent and trivalent actinides, respectively. Cerium (Ce) is used to study the behavior of plutonium, since both elements can exist in the glass in trivalent or tetravalent form. Preliminary results are presented from studies of the evolution of the solubility of these actinide surrogates with the process temperature and the redox potential of the melt.

2. Work description

The study was performed with a borosilicate glass containing the following components (in wt%), SiO_2 58.84; B_2O_3 18.15; Na_2O_7; Al_2O_3 4.28; CaO 5.23; Li_2O 2.56; ZnO 3.24; ZrO_2 0.70. The solubility limits of the actinide surrogates were determined at processing

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temperature of 1100, 1200, 1300, and 1400 °C. The glass samples were melted in air, in zirconia crucibles from a mixture of powder precursors (oxides, nitrates, or carbonates) or from pre-processed and ground glass frit. Cerium, hafnium, and neodymium were added as sieved CeO_2, HfO_2, and Nd_2O_3 powders. The melts were maintained for three hours at the process temperature to ensure homogenization. The crucible was then removed from the hot furnace to prevent crystallization during cooling. The cooling rate is ranging from 100 °C/min at the beginning, to 10 °C/min at the end, of the cooling process. Other glass samples were melted under reducing conditions at 1200 °C in argon atmosphere by adding a reducing agent (aluminum nitride) to the melt.

The solubility of the actinide surrogates was defined in this study as the maximum surrogate concentration that could be incorporated into the glass. The glass samples were therefore produced by gradually increasing the surrogate concentrations to their loading limits, above which crystallization and/or phase separation were observed.

The glass homogeneity was characterized by optical and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) microanalysis. X-ray diffraction was also used to identify any crystalline phases in the amorphous matrix. Glass specimens containing cerium were also characterized by transmission electron microscopy (TEM) and by small-angle-X-ray scattering (SAXS) to verify the material homogeneity at a smaller scale (nanometric scale) than by SEM (micrometric scale). The cerium oxidation state in the glass was determined by cerium L_{III}-edge XANES (X-ray absorption near-edge structure) spectroscopy performed at the Orsay Electromagnetic Radiation Application Laboratory, and by chemical titration.

3. Results

The evolution of the Ce, Hf, and Nd solubility in the borosilicate glass was determined for processing temperatures ranging from 1100 to 1400 °C. The experimentally measured solubility limit S for each actinide surrogate (Table 1) ranged between a lower limit corresponding to the maximum quantity of surrogate that could be incorporated in the glass matrix while maintaining its homogeneity, and an upper limit corresponding to the quantity above which the first heterogeneities were observed. These limits can be considered as the precision of the solubility measurement.

3.1. Cerium solubility

Above the cerium solubility limit, optical and SEM observations revealed the presence of whitish aggregates several hundred micrometers across (Fig. 1(a)) at the bottom of the specimen (i.e., near the interface between the glass and the bottom of the crucible). They consisted of small (micrometer-scale) cubic crystals. EDS analysis showed that the crystals contained Ce and O, and they were identified by X-ray diffraction as CeO_2. Homogeneous Ce-doped borosilicate glasses made at various temperatures were also characterized by TEM observation and SAXS. The results revealed no evidence for Ce crystals and so confirmed that Ce is completely solubilized in the glass matrix.

The cerium oxidation state in glasses elaborated in air was determined by chemical titration. The results showed that the glass contained a mixture of Ce^{3+} and Ce^{4+}, and that the trivalent cerium fraction increased from 53.8% to 88.1% of the total cerium as the glass making temperature rose from 1100 to 1400 °C (Table 2).

For the glass melted at 1200 °C in air, the Ce solubility limit was between 3 and 4 wt% Ce_2O_3. At the same temperature, but under an argon atmosphere with aluminum nitride added to the melt, the Ce solubility limit increased to 13–14 wt% Ce_2O_3; cerium silicate crystals were detected by SEM for higher Ce_2O_3 loading (Fig. 2(a)). Phase separation was observed in the glass above 20 wt% Ce_2O_3 (Fig. 2(b)). This phenomenon was also observed in the Nd doped glass (see paragraph 3.3). Borosilicate glass specimens containing 4, 6, and 8 wt% Ce_2O_3 melted under an argon atmosphere with aluminum nitride addition, were characterized by XANES spectroscopy. The spectra of a Ce^{3+} reference compound

Table 1
Solubility limits of actinide surrogates (Ce, Hf, and Nd) determined in a borosilicate glass between 1100 and 1400 °C

Temperature (°C)	Ce solubility limits (Ce_2O_3 wt%)	Hf solubility limits (HfO_2 wt%)	Nd solubility limits (Nd_2O_3 wt%)
1100	$0.5^a < S < 1^b$	$1^a < S < 1.5^b$	$8^a < S < 10^b$
1200	$3^a < S < 4^b$	$1^a < S < 1.5^b$	$19^a < S < 20^b$
1300	$6^a < S < 6.75^b$	$2^a < S < 3^b$	$20^a < S < 22.5^c$
1400	$16^a < S < 17^b$	$4^a < S < 5^b$	$20^a < S < 22.5^c$

[a] Homogeneous glass.
[b] Glass containing crystals.
[c] Phase-separated glass.

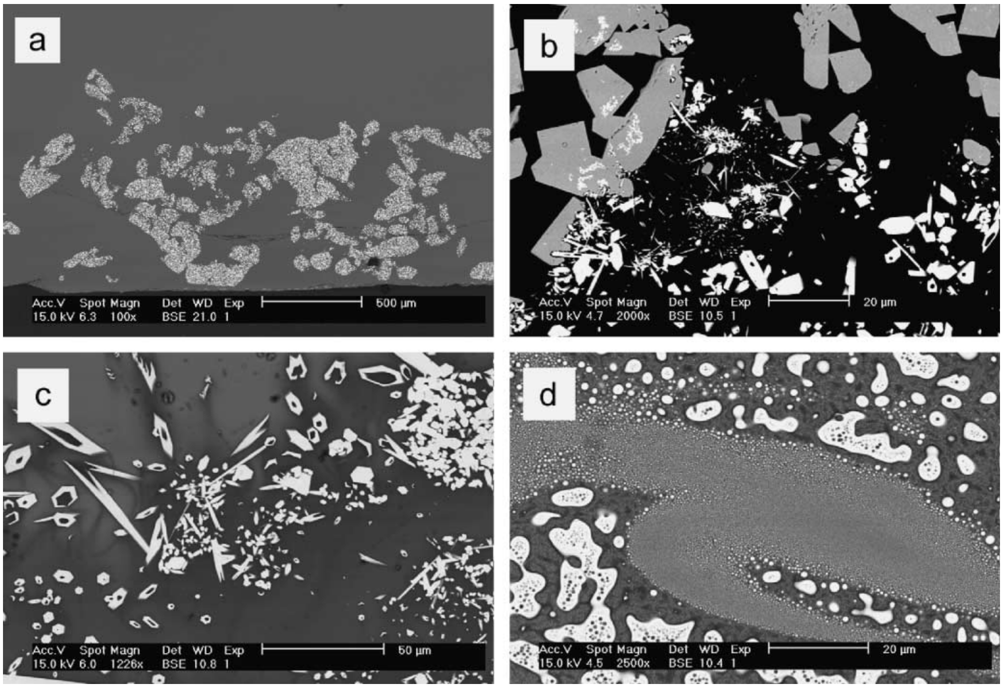

Fig. 1. Scanning electron micrographs of heterogeneities observed in borosilicate glass above the solubility limits for Ce (a), Hf (b) and Nd (c,d).

Table 2
Cerium oxidation state (determined by chemical titration) versus borosilicate glass processing temperature

Temperature (°C)	Ce^{3+}/Ce_{total} (%)
1100	53.8 ± 0.6
1200	67.7 ± 1.3
1300	78.8 ± 0.3
1400	88.1 ± 0.3

($Ce(NO_3)_3$, $6H_2O$), and a Ce^{4+} reference compound (CeO_2) were used. The experimental glass spectra were comparable to the Ce^{3+} reference spectrum, indicating complete reduction of cerium in these glass samples (Fig. 3).

3.2. Hafnium solubility

Two types of heterogeneities were observed in glass containing hafnium (Fig. 1(b)): white hafnium oxide crystals and gray hafnium silicate crystals, which were also found at the bottom of the glass sample. The HfO_2 and $HfSiO_4$ phases were identified by X-ray diffraction.

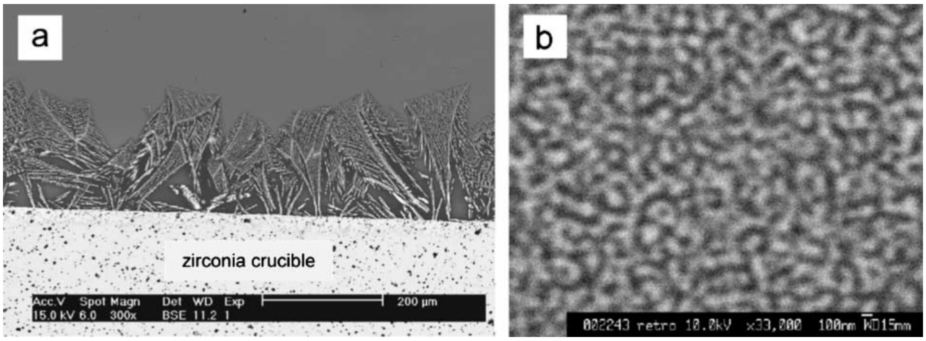

Fig. 2. SEM image of cerium silicate crystals (a) and phase separation (b) in glass containing 20 wt% Ce_2O_3. EDS analysis showed that one of the vitreous phases (the white phase) was enriched in Ce.

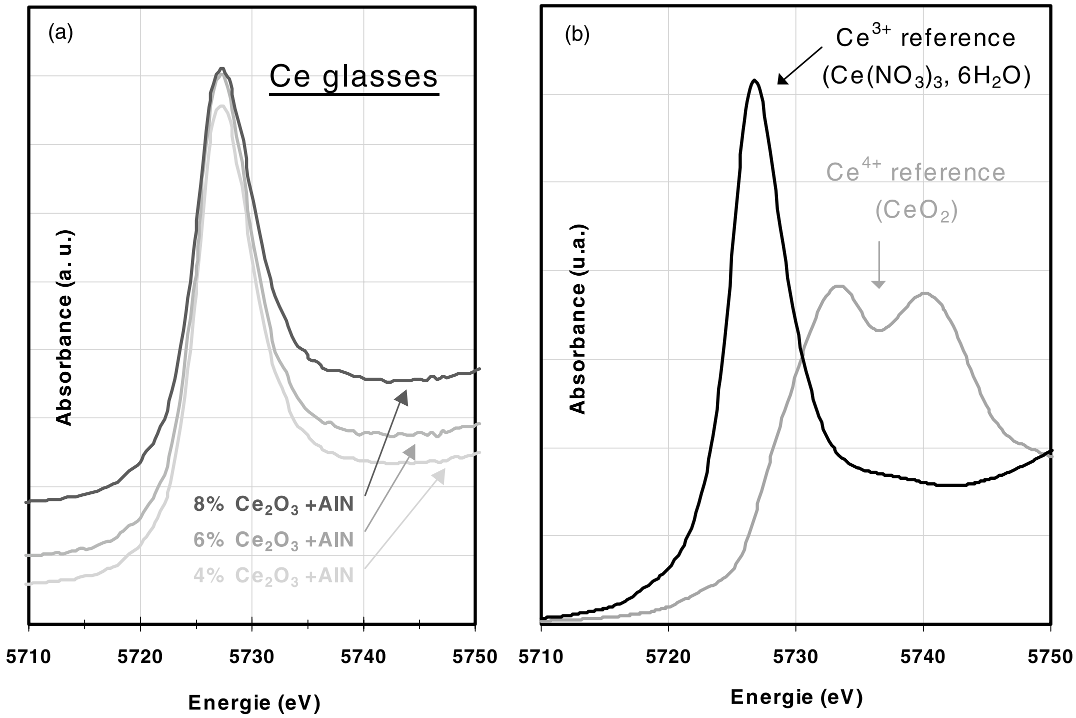

Fig. 3. XANES spectra of borosilicate glass containing 4, 6, and 8 wt% Ce_2O_3 melted in argon with aluminum nitride (a) compared with the spectra of the reference compounds for Ce^{3+} ($Ce(NO_3)_3$, $6H_2O$) and Ce^{4+} (CeO_2) (b). The experimental glass spectra are comparable to that of the Ce^{3+} reference compound, indicating that all the Ce in the glass was reduced.

3.3. Neodymium solubility

The neodymium-doped glass specimens melted at 1100 and 1200 °C contained neodymium silicate crystals when the loading limits for Nd were exceeded (Fig. 1(c)). In the samples melted at temperatures of 1300 °C or above, however, opalescent zones appeared at Nd_2O_3 concentrations exceeding 20 wt%, while the first Nd silicates were detected only above 35 wt% Nd_2O_3. SEM observations showed that the opalescence was due to phase separation: one of the two vitreous phases (white phases in Fig. 1(d)) was enriched in Nd. We consider that the glass is no longer homogeneous when this separation occurs, because the Nd distribution in the material is no longer homogeneous.

4. Discussion and conclusion

The experimental results show an increase in the solubility of the actinide surrogates with the glass melting temperature. The greatest increase in solubility was observed with cerium: the Ce^{3+}/Ce_{total} ratio in the glass indicated that the Ce^{3+} fraction increased with the processing temperature. From a thermodynamic standpoint, Paul [1] used the Van't Hoff law (which predicts the temperature effect on the direction of a reaction) to demonstrate that a temperature increase shifts the redox equilibria toward the reduced species. The higher Ce^{3+} content enhances the cerium total solubility since, as shown by Li et al. [2] Ce^{3+} is more soluble in glass than Ce^{4+}. In borosilicate glass melted in air at 1200 °C, the Ce solubility limit ranges from 3 to 4 wt% Ce_2O_3 and the glass contains about 68% Ce^{3+}. We also prepared glass samples at 1200 °C under reducing conditions with aluminum nitride added to the melt in order to obtain glass containing only Ce^{3+}. The free energy values were calculated by Diaz et al. [3] for different possible Ce reduction reactions by AlN; the lowest – and therefore most likely – $\Delta G°$ value was obtained for the following reaction:

$$3Ce^{4+} + N^{3-} \rightarrow 3Ce^{3+} + 1/2N_2. \qquad (1)$$

Gas bubbles were effectively observed during the making of the samples containing aluminum nitride. Glass specimens melted under reducing conditions can accommodate Ce loading of more than 13 wt% Ce_2O_3. XANES characterization of the samples confirmed that the increased Ce solubility was due to complete reduction of all the cerium in the glass.

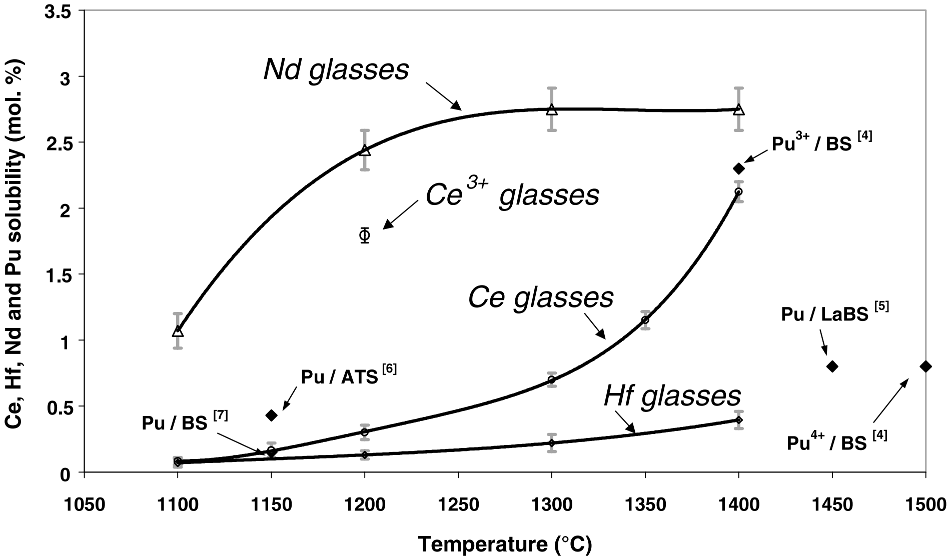

Fig. 4. Ce, Hf, and Nd solubility limits (mol.%) determined experimentally in a borosilicate glass. The solubility limits of these actinide surrogates are compared with published data concerning Pu solubility in various borosilicate glass compositions [4–7].

We compared the experimentally measured solubility limits of the actinide surrogates in our borosilicate glass with published data on Pu solubility in various borosilicate glasses [4–7]. The surrogate concentrations are expressed as a molar percentage because comparisons of the solubility limits of different elements are more relevant in terms of the number of atoms incorporated into the glass network than by weight. Fig. 4 shows that at low processing temperatures (1100–1200 °C), plutonium, cerium, and hafnium are sparingly soluble with comparable loading factors in borosilicate glass. At higher processing temperatures (1300–1400 °C), the solubility of Pu^{4+} is similar to that of Hf^{4+}, and the solubility of Pu^{3+} is comparable to that of Nd^{3+} and Ce^{3+} (since about 90% of the cerium is found as Ce^{3+} at 1400 °C). The results also clearly show that Pu and its surrogates are more soluble in trivalent than in tetravalent form.

A study is currently in progress to determine the solubility of the actinides in borosilicate glasses. One aspect of this work concerns an EXAFS investigation of the atomic environment of the actinides and their surrogates in the glass. Determining the local and chemical structure around these elements should provide better understanding of their structural role in the glass and an explanation for the observed solubility differences.

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