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EXAFS STUDIES OF SODIUM SILICATE GLASSES CONTAINING DISSOLVED ACTINIDES*

G. S. Knapp, B. W. Veal, A. P. Paulikas, A. W. Mitchell,
D. J. Lam, and T. E. Klippert
Materials Science and Technology Division
Argonne National Laboratory
Argonne, IL 60439

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T. E. Klippert, Materials Science and Technology Division, Argonne
National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

MASTER

Abstract

Sodium silicate glasses containing dissolved Th, U, Np, and Pu have been studied using the EXAFS technique. Th⁴⁺, U⁴⁺, Np⁴⁺, and Pu⁴⁺ ions in the silicate glasses are 8-fold coordinated to oxygen neighbors. The higher valent U⁶⁺ and Np⁵⁺ ions have complex local symmetries. The U⁶⁺ ions appear in a uranyl configuration with 2 oxygen atoms at 1.85Å and 4 at 2.25Å from the U ion. The Np⁵⁺ local symmetry is more complex and difficult to determine uniquely. The U⁶⁺ glasses show substantial clustering of the uranium atoms. A structural model, with nearly planar uranyl sheets sandwiched between alkali and silica layers, is used to explain the U⁶⁺ EXAFS data. This model allows us to understand why U⁶⁺ ions are much more soluble in the glasses than the actinide 4⁺ ions.

The bonding properties of actinide elements in silicate glasses are of current interest because such glasses are being considered as storage media for radioactive wastes. Solubility measurements show that the bonding depends strongly on valence and type of the actinide ions. For example, when Th, U, Np, or Pu are in the 4+ state the solubility is quite low (less than 5%).¹ However U⁶⁺ and Np⁵⁺ exhibit much greater solubilities, being 30% in the case of U⁶⁺ and 10% for Np⁵⁺. We have made EXAFS measurements on a number of sodium disilicate and trisilicate glasses containing various actinides in different charge states, and have found that U⁶⁺ and Np⁵⁺ bond quite differently than 4+ ions.

The EXAFS measurements were made using our laboratory EXAFS facility. [1,2] Both Si(620) and Si(840) bent crystals were used. Resolution varied depending on the absorption edge studied but was always better than 17 volts. Deconvolution procedures were used to minimize the effects of the low resolution. All measurements reported here were made at temperatures between 79 and 84K and all samples were powders encapsulated in polyethylene. The glasses were made by methods described earlier, [3] except the 4+ glasses which were made in a reducing atmosphere. The data were analyzed using the standard EXAFS equation, with the phase shifts and amplitudes determined from the corresponding dioxides. [4]

In an earlier work we made a detailed study of some U⁶⁺ glasses. [3] In Fig. 1 we show kχ(k) versus k for a series of these U⁶⁺ glasses. Note the large amplitude oscillations at high k which vary as a function of composition. From this composition, amplitude, phase, and temperature

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¹Here we define the % concentration as 100x, where x is defined from the formula (0.25Na₂O·0.75SiO₂)_{1-x}(AnO)_x and An stands for an actinide.

dependence (heavy atoms have low Einstein temperatures), we concluded that these oscillations resulted from uranium containing clusters. The uranium bonds in a uranyl configuration (a linear UO_2^{2+} ion) with two oxygen atoms at 1.85 Å and four at 2.25 Å, and as many as four uranium atoms at approximately 3.3 Å. The large U backscattering intensity suggests extensive U clustering. By making a simple planar model (see below) we concluded that the clusters, on the average, must contain at least six uranium atoms.

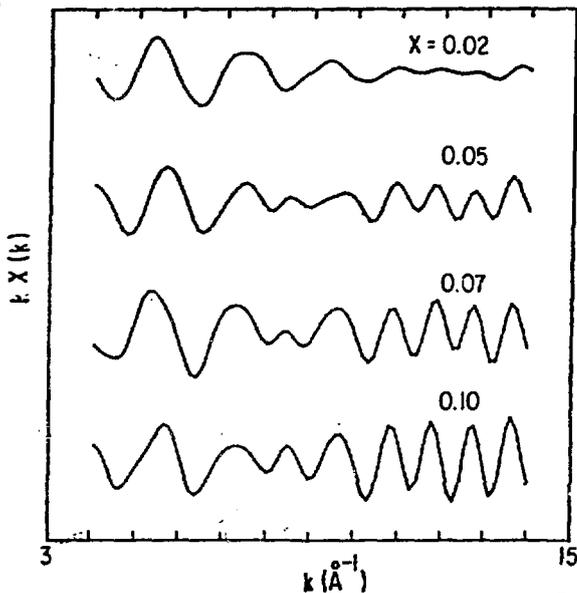


Fig. 1. Experimental EXAFS spectra for a series of sodium trisilicate glasses contain UO_2^{+} ions at various concentrations, measured at approximately 80K

The glasses containing the 4+ ions have a very different local environment. In Fig. 2(a) and 2(b) we show the radial distribution functions of PuO_2 and a 1.5% Pu glass. Note that the oxygen shell peak is virtually identical to that of the PuO_2 . Since the radial distribution function is a sensitive function of both the numbers of neighbors and their local symmetry, this means that the local environment is nearly identical out to the first near neighbor. Results of nonlinear least-squares fitting confirm this, the only difference being that the Pu-O distance is slightly smaller in the glass. The other 4+ glasses are very similar. There are 8 ± 1 oxygen near-neighbor atoms at a distance which is slightly smaller than the distance in the corresponding dioxides.

The Np^{5+} glasses are more complex. In Fig. 2(c) and 2(d) we show the radial distribution functions of NpO_2 and a 2% Np^{5+} glass. Note the striking differences in the first neighbor peaks. Nonlinear least-squares fits with one-shell and two-shell models have been attempted for several of these glasses but no satisfactory fits have been achieved. The average distance is much smaller than that of NpO_2 and the number of neighbors is smaller.

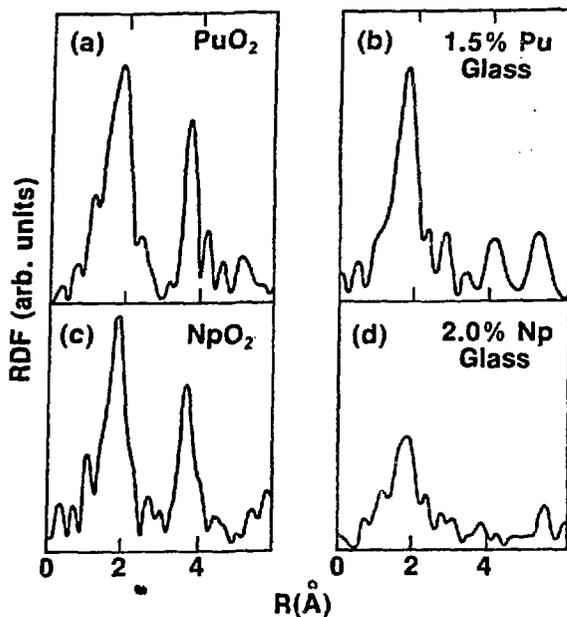


Fig. 2. The radial distribution functions (at ~ 80K) of (a) PuO_2 , and (b) a Pu^{4+} glass with $x \approx 0.015$, (c) NpO_2 , and (d) a Np^{5+} glass with $x = 0.02$

How are we to understand these results and how do we understand the differences in solubilities? First consider the U^{6+} glasses. The local symmetry is that of the uranyles, which in their crystalline forms can be considered as layered compounds in which the U and O are in layers, separated by weakly bonding alkali ions. Crystalline sodium silicates are also layered compounds with corner-bonded double silicate layers separated by sodium ions. We previously proposed a model in which the uranyl clusters are almost planar, between silica layers. The $4+$ ions, on the other hand, are 8-fold coordinated in a locally cubic symmetry (in analogy with the CaF_2 structure of the actinide dioxides). In order to have eight near-neighbor oxygen atoms coordinated with the actinide ions, the Na ions have to be displaced and the silicate network has to be highly distorted and strained. This is why the solubility is low. The Np^{5+} glasses may be more similar to the U^{6+} glasses. However the results are more complex and more work is necessary for full understanding.

References

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4. For a good review of the EXAFS technique, see P.A. Lee, P.H. Citrin, P. Eisenberger, and B.M. Kincaid, Rev. Mod. Phys. 53 (1981) 769.