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Project #81926

Chemistry Of Actinides In Molten Glasses And Its Correlation To Structural Performance Of Solid Glasses: *Filling A Knowledge Gap*

S. Dai,[1] S. M. Mahurin,[1] L. A. Boatner,[2] R. F. Schumacher,[3] and C. E. Barnes[4]

[1]Chemical Sciences Division, [2]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831; [3]Westinghouse Savannah River Company, Aiken, South Carolina, 29808; [4]Department of Chemistry, the University of Tennessee, Knoxville, TN 37996

Background

Borosilicate glass are the primary matrices to be used in the immobilization of high-level nuclear waste (HLW). To understand the current immobilization process properly and design new immobilization systems, we must develop an atomic level understanding of these systems which involves the chemical bonding present in these materials. The work proposed here specifically addresses needs for

- fundamental chemical studies of actinides in glasses,
- determination of radionuclide species in molten glass solutions, and
- development of a predictive theory describing the properties of actinide- doped glasses.

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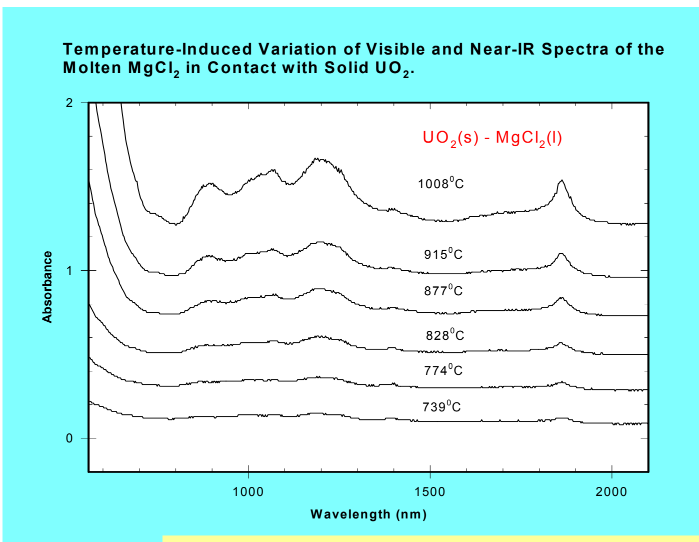
Objectives

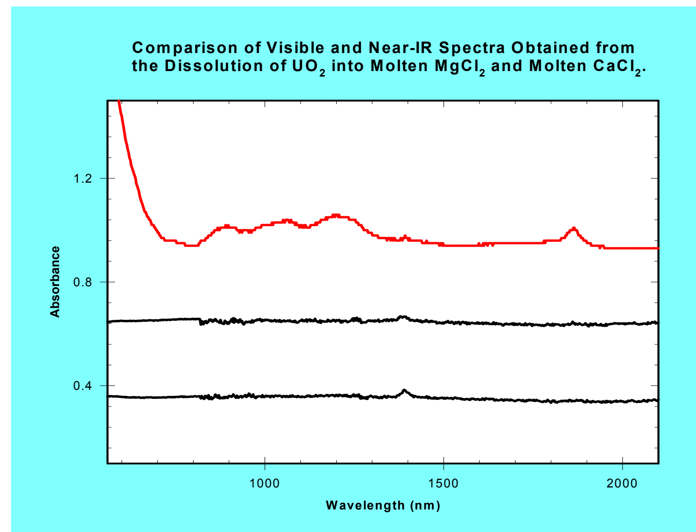
(a) Develop speciation techniques for actinides in *molten glasses*;
(b) Develop a *spectral fingerprints* for the nanoscale phase segregation in immobilization process;
(c) Develop a new "*optical pH*" scale relating actinide complex identity to the composition and oxidic character of a glass;
(d) Correlate key spectral *fingerprints* to leaching rates and stabilities of actinides species in glass matrices.

We can draw upon our extensive and unique expertise from past and present research programs on high temperature molten salt-chemistry to address this complex area, which could open new avenues for the design of efficient vitrification processes. The understanding developed in this work will be directly applied to the vitrification task at Savannah River Site and will provide the basis for improved approaches for the efficient vitrification processes. The work will be closely coupled to the needs of the vitrification efforts at Savannah River, Hanford, Oak Ridge, and Idaho sites.

Our Prior High-Temperature Spectroscopic Characterization of Actinides in Molten Salts



Temperature-Induced Variation of Visible and Near-IR Spectra of the Molten $MgCl_2$ in Contact with Solid UO_2.



Comparison of Visible and Near-IR Spectra Obtained from the Dissolution of UO_2 into Molten $MgCl_2$ and Molten $CaCl_2$.

Solubilities of UO_2 in Molten $MgCl_2$ and $CaCl_2$

No Solubility in $CaCl_2$ | **High Solubility in $MgCl_2$**

(a) S. Dai, L. M. Toth, G. R. Hayes, and J.R. Peterson, *Inorg. Chim. Acta*, **1997**, *256*, 143. (b) S. Dai, L. M. Toth, G. D. Del Cul and D. H. Metcalf, *J. Phys. Chem.*, **1996**, *100*, 220.

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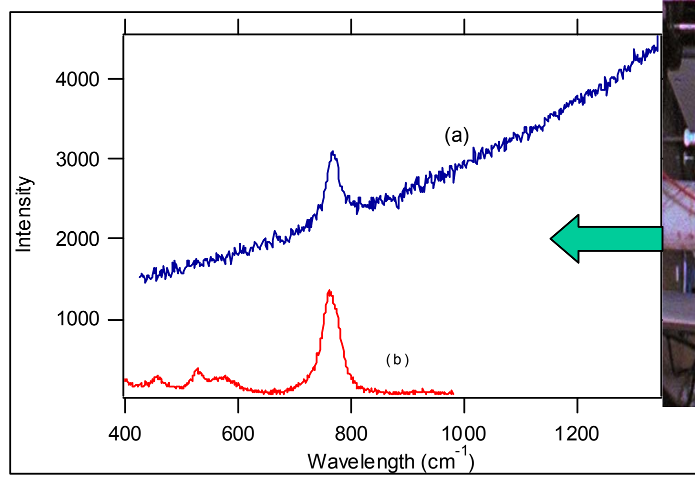
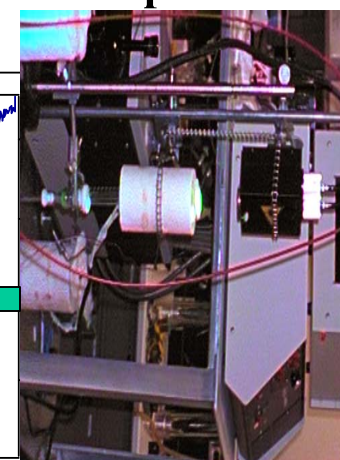
NEW High-Temperature Raman Spectroscopy of Uranyl Ions in Molten Glasses

- First Raman spectroscopic measurement of uranyl ions in molten glasses
- Potential applications in remote sensing for immobilization processes



Fiberoptic Raman



Raman spectra of uranyl in borosilicate glass (a) at 950°C and (b) at room temperature after heating at 1000°C for 16 hours.

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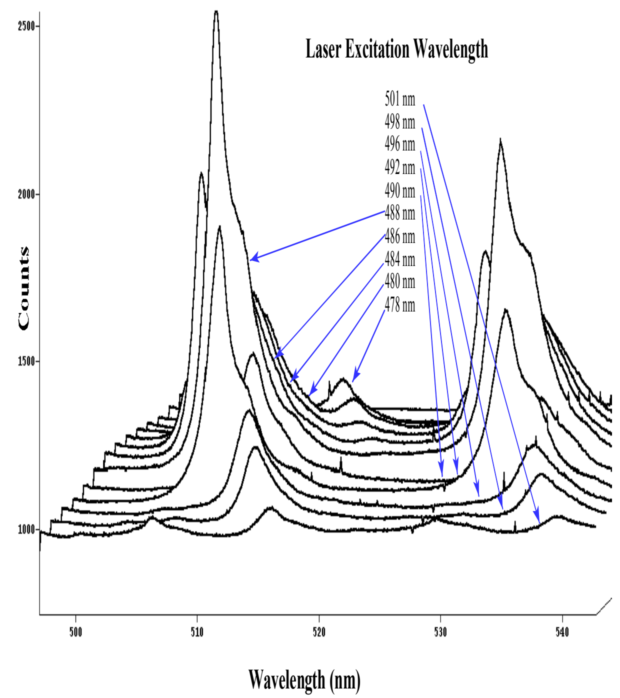
Site-Selective Spectra of Uranyl Ions in Silica Glass at 77 K

- Heterogeneity for sites of uranyl ions
- Structural probes for interaction of uranyl ions with matrixes



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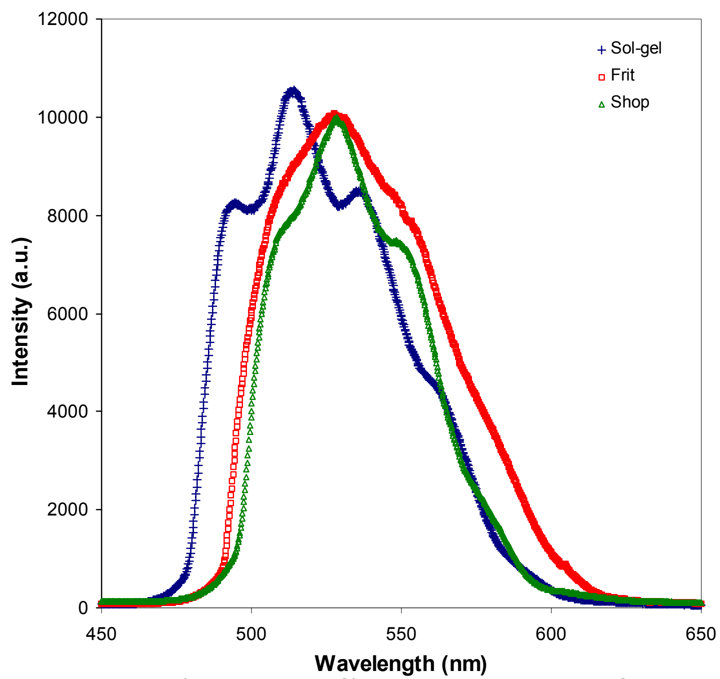
Comparison of Fluorescence Spectra for Three Silica-Based Glasses Prepared Under Different Conditions

- This sharp difference in the position of maximum emission between the high-temperature and sol-gel glasses indicates that the bonding of uranyl ions is very different in the sol-gel glass from those in the high-temperature glasses.

- Different heterogeneity of two high-temperature glasses.



Steady-state fluorescence of uranyl in three glasses

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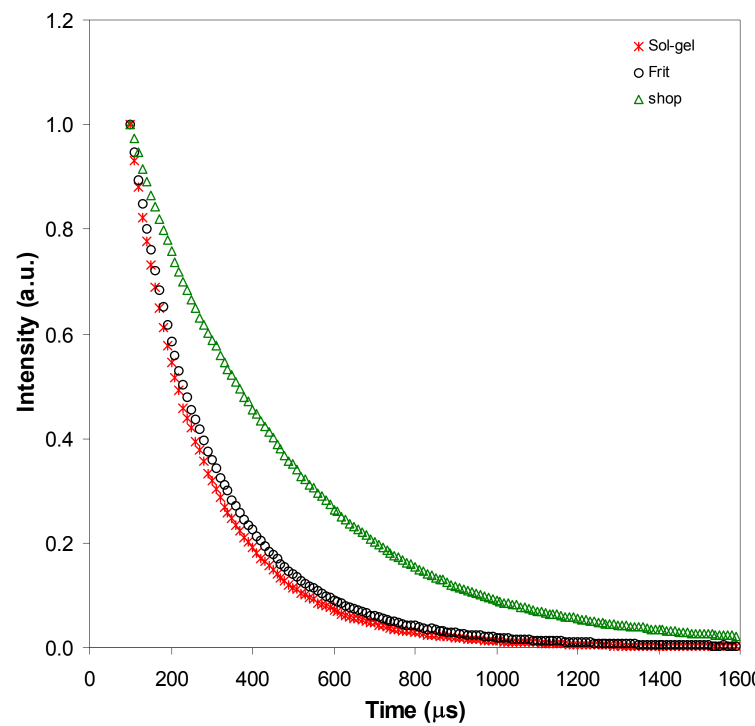
Fluorescence Decay For Uranyl In Three Types Of Glass

- Nonlinear decays
- Different lifetimes

A continuous distribution of species is normally present in an amorphous glass. This type of distribution is mathematically represented by an integral equation of the form:

$$I(t) = \int_{0}^{a} e^{-t/\tau} s(\tau) d\tau$$



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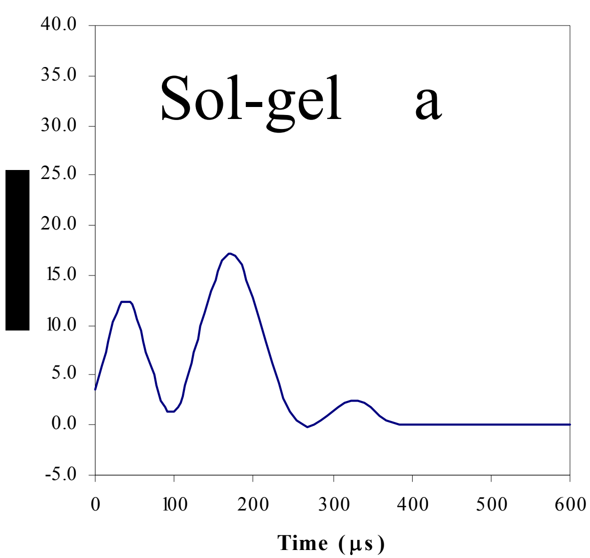
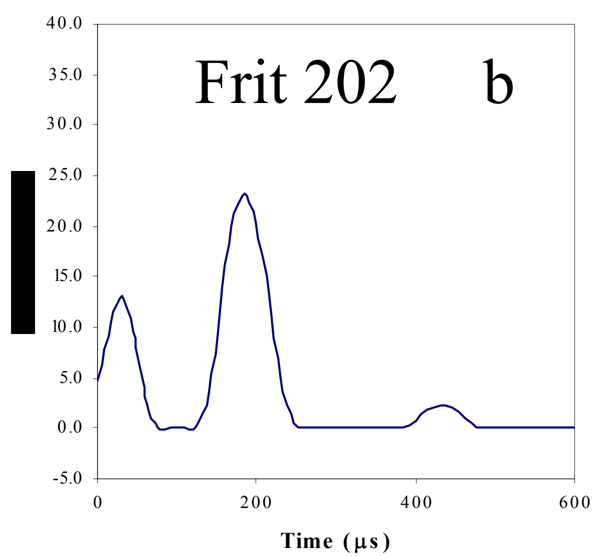
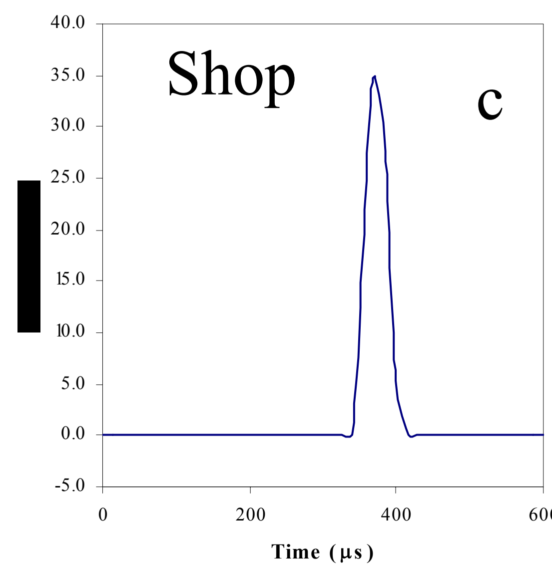
Lifetime distributions determined using CONTIN methodology for uranyl ions in a) sol-gel glass, b) frit, c) commercial glass



Uranyl in Multiple Domains



Uranyl in Multiple Domains



Uranyl in One Domain

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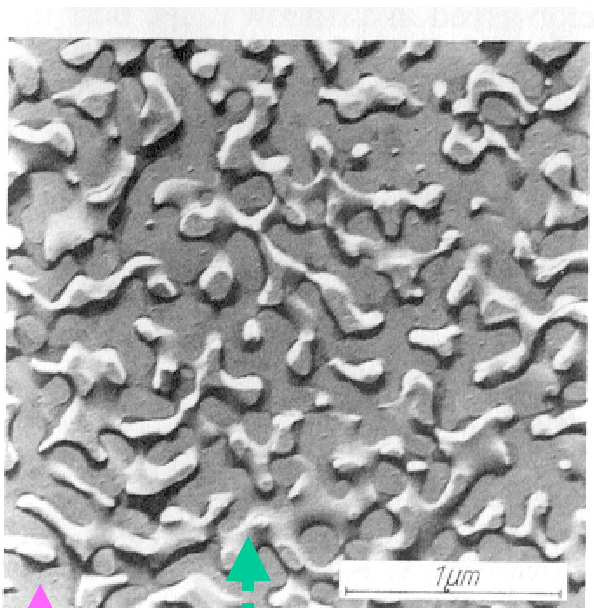
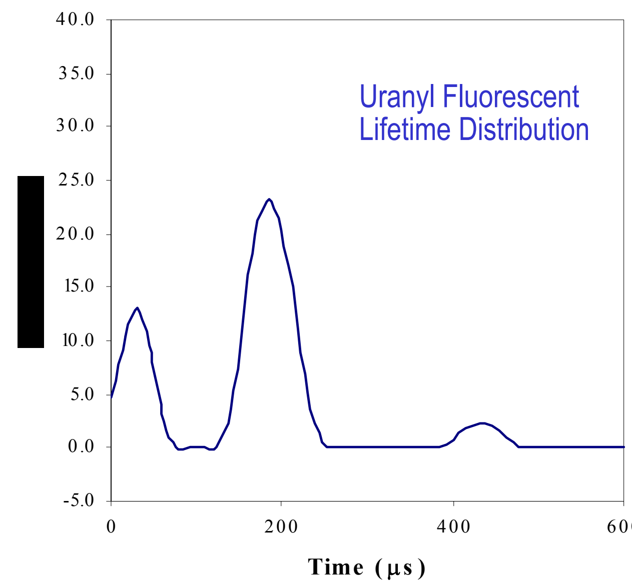
Nanoscale Phase Segregation in Borosilicate Glass



Spectral Probe For Phase Segregation



Boron-Rich Phase

Silica-Rich Phase

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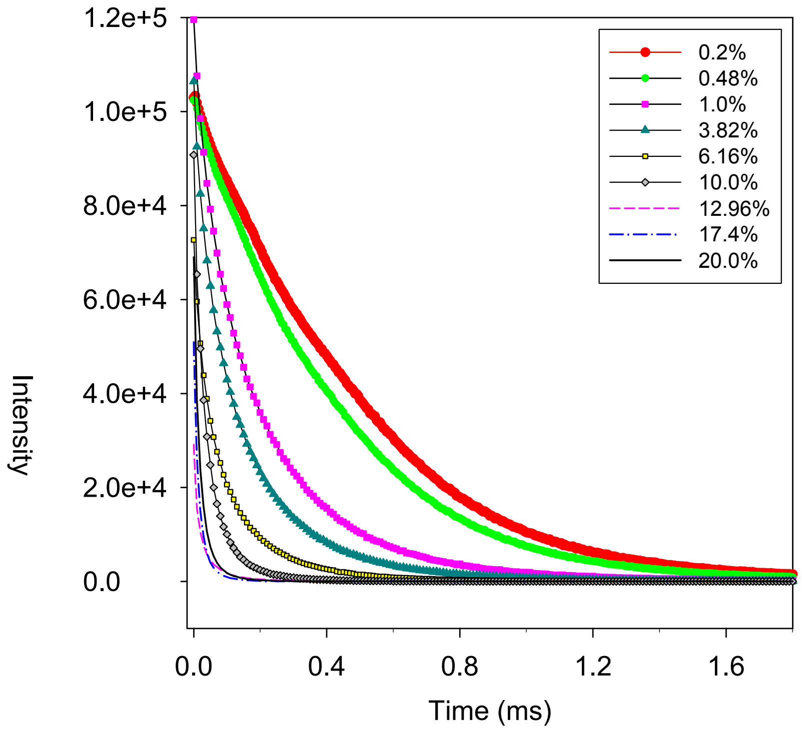
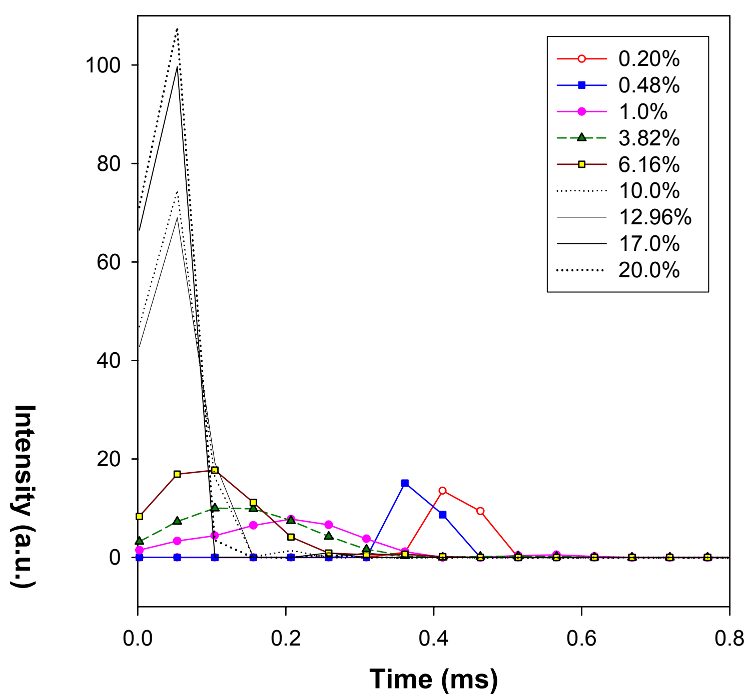
Decay Curves Measured as Function of Uranium Concentration

Decay Curves



Lifetime Distributions



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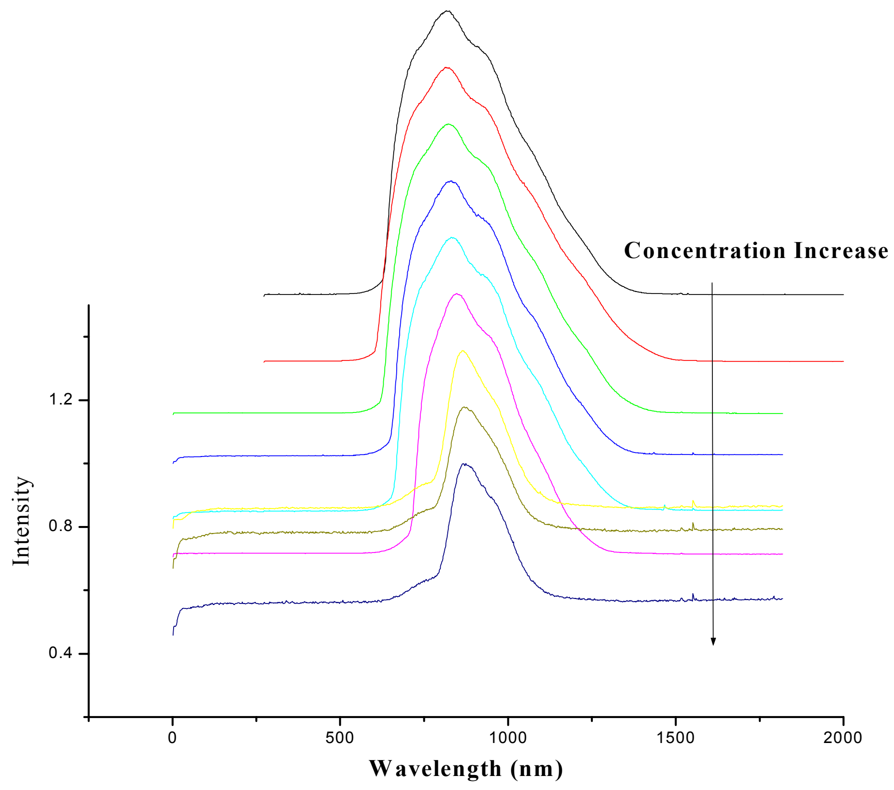
Uranyl Fluorescence Spectra as Function of Concentration



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Acidity and Basicity for Oxides "pH"

In the theory developed by Lux and Flood,[a, b] an oxidic molten silicate is characterized by the following dissociations relevant to oxide activity and basicity:

SiO_3^{2-} ✧ $SiO_2 + O^{2-}$

SiO_4^{4-} ✧ $SiO_3^{2-} + O^{2-}$

(a) Lux, H. Z. "Sauren Und Basen in Schmelzfluss: Die Bestimmung Der Sauerstoffionen-Konzentration" *Electrochem.* **1939**, *45*, 303; (b) Flood, H. and Forland, T. "The Acidic and Basic Properties of Oxides" *Acta Chem. Scand*. **1947**, *1*, 592.

In-situ Optical Basicity
"pH" of Solid State Glasses

Metal ions such as Tl^{+}, Pb^{2+}, and Bi^{3+} have been employed as optical probes to measure the basicity of industrially-interesting oxide glasses. The ratio of the nephelauxetic parameter of a probe ion for a particular oxidic system to that for an ionic oxide (usually CaO) is known as the optical basicity, .

🖮 = (🖫$_{f}$ - 🖫)/ (🖫$_{f}$ - 🖫$_{CaO}$)

where 🖫 $_{f}$ is a specific electronic transition energy of the free, uncoordinated probe ion, and 🖫$_{CaO}$ is the frequency for the probe ion in CaO. Our objectives are to

- Determine spectral shifts of actinide species (U(IV), U(VI), U(V)) in solid glasses as function of the Lewis basicity;
- Correlate spectral shifts with local basicity and calculate optical basicity parameters for the actinide species.

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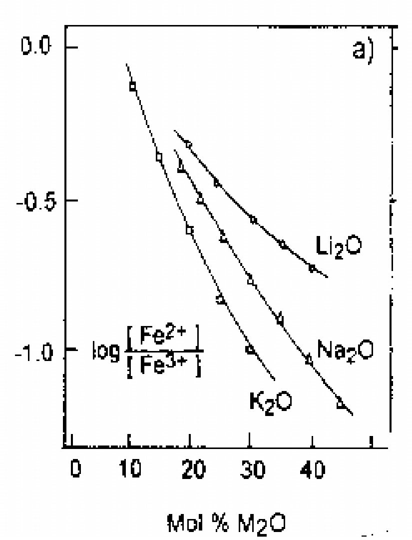
Redox Chemistry of Uranium Species in Molten Glasses

(1) Determination of the variation of valent states of actinide species in molten glasses obtained by dissolution of UO_2 and U_3O_8 as function of the Lewis basicity of the melts under inert atmospheres;

(2) Determination of the variation of valent states of actinide species in molten glasses obtained by dissolution of UO_2, U_3O_8 as function of O_2 concentration above the melts.



Example of dependence of solute valent states on oxide basicity.

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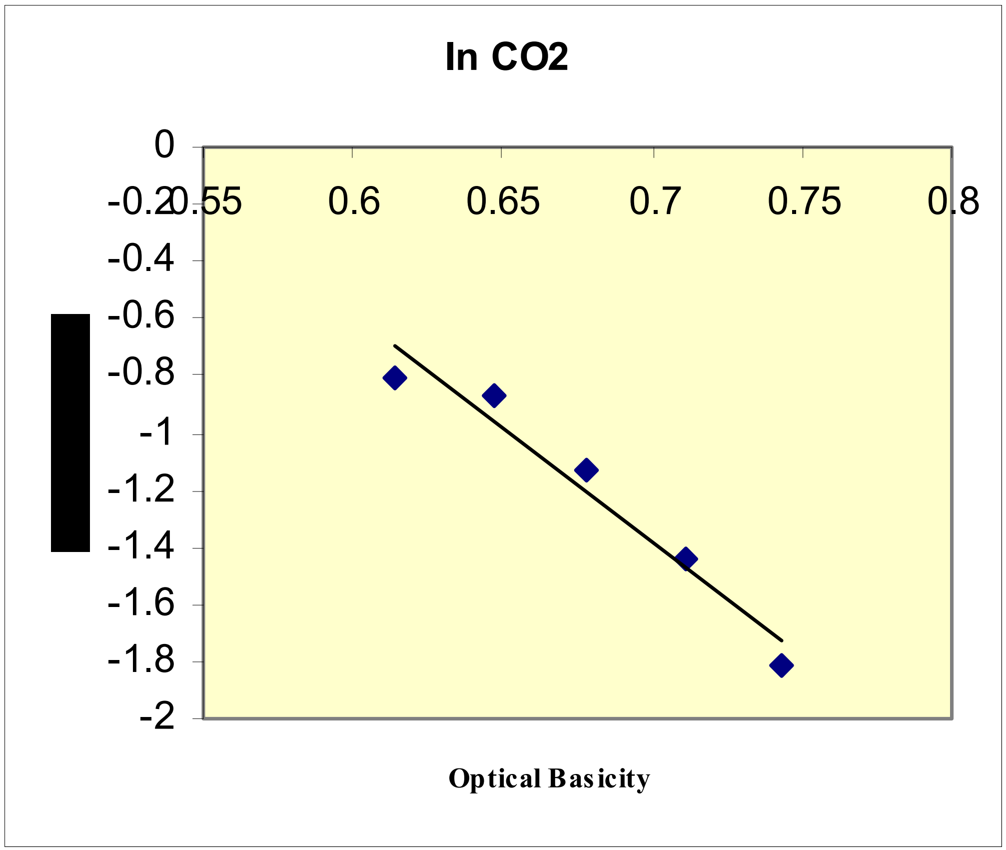
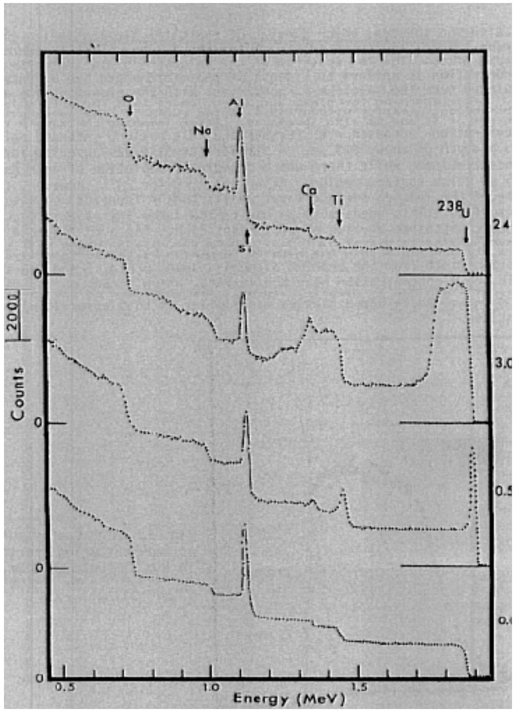
Correlation of Optical "pH" with Valent States



Rutherford Backscattering Applied to Glass Corrosion

We propose to employ the technique of RBS analysis and ion implantation combined with RBS analysis in conjunction with the other experimental techniques described in the present proposal to achieve a new level of understanding of the relationship between nuclear waste glass composition and solid state chemical properties and the waste glass stability when exposed to aqueous conditions.



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Collaboration

Dr. Sheng Dai is a staff scientist of the Chemical Technology Division at ORNL. He will be responsible for spectroscopy of actinides in molten glasses, development of optical basicity for actinide-doped glasses, fluorescence spectroscopy, and chemometrics in this project. His present research interests include chemistry of actinides and fission products, high-temperature molten salts, advanced sol-gel glass materials, chemical sensing via molecular recognition, and fiber-optic instrumentation.

Dr. L. A. Boatner is a Corporate Fellow at the Oak Ridge National Laboratory (ORNL) and is the Head of the Ceramics and Interfaces Section in ORNL's Solid State Division. His research activities have included investigations of the static and dynamic Jahn-Teller effect, electron paramagnetic resonance studies of rare-earth, iron-troup, and actinide ions in crystalline materials, the growth and properties of ferroelectric thin films, the development and characterization of advanced nuclear waste forms, the application of Rutherford backscattering to glass corrosion, the growth of single crystals, and ion-damage and epitaxial-regrowth studies of insulating oxides.

Dr. Ray F. Schumacher is a senior fellow scientist at Westinghouse Savannah River Company. He has extensive experiences in vitrification of Hanford RPP, HLW glasses in the shielded cells and formulation of glass compositions for vitrification of high-level wastes. He will help to interpret spectral data and formulate glass composition for our high-temperature spectroscopy studies.

Dr. Craig E. Barnes is an associate professor of chemistry at UTK. His group at UTK will be responsible to conduct development of optical basicity for actinide-doped glasses in this project.

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Relevance

1. Borosilicate glasses are the primary matrixes used in the immobilization of high-level nuclear wastes. Although there are several prior EMSP research programs targeted for understanding solid behaviors of borosilicate matrixes, ***no research*** has been initiated to understand the chemistry of **molten glasses**.
2. Chemical processes occurring in molten glasses are key elements in determining efficient immobilization and the long term stability of glasses. Confidence and assurance that long-term immobilization will be successful warrants research and improved understanding of the structural and thermodynamic properties of molten glasses.
3. The underlying goal of the proposed research is to make use of our high-temperature spectroscopic techniques to increase our fundamental understanding of the vitrification processes and bridge the gap between glass melt model data and melter performance. The understanding developed in this work will be directly applied to the vitrification task at Savannah River Site and will provide the basis for improved approaches for the efficient vitrification processes.
4. The work will be closely coupled to the needs of the vitrification efforts at Savannah River, Hanford, Oak Ridge, and Idaho sites.

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Implementation

1. Conduct optical spectral investigation of actinide species in molten glasses.
2. Establish a protocol to determine solubilities of actinide species in molten glasses as function of Lewis basicity.
3. Explore the possibility to determine the optical basicities of glasses by use of optical spectra of uranyl ion or U(V).
4. Determine redox properties of actinide species in glasses as function of Lewis basicity.
5. Probe the site distribution of actinide species in glasses via fluorescence lifetime distribution method.
6. Correlate the above spectral fingerprints to leaching test.
7. Technology transfer of results to ongoing activities at SRS.