

# Tuesday Afternoon, October 19, 2010

## Actinides and Rare Earths Topical Conference

Room: Isleta - Session AC-TuA

### Science and Technology of Actinides and Rare Earths

Moderator: R.K. Schulze, Los Alamos National Laboratory

2:00pm **AC-TuA1 Enhanced Photoluminescence from Europium-Doped Gadolinium-Based Nanocrystal Scintillators**, *T.-K. Tseng, J. Choi, M.R. Davidson, P.H. Holloway*, University of Florida

Scintillator crystals have traditionally been grown with complex single crystal methods such as Czochralski and Bridgman techniques, which frequently result in high costs and small crystal size. Therefore, development of processes for larger area, polycrystalline ceramic scintillators with high luminescence is of great interest due to their potential for mass production, versatility in shape and size, and low cost. In this study, spherical  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  and almond-like  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals were synthesized using a water-based solution precipitation method at low reaction temperatures ( $<90^\circ\text{C}$ ) in short times (3 min~1 h). Core/Shell nanostructures with mono-dispersed 220 nm  $\text{SiO}_2$  cores and an ~13 nm  $\text{Gd}_2\text{O}_3$  shell, i.e.  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ , were prepared. With an additional undoped  $\text{Gd}_2\text{O}_3$  shell to form a  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Gd}_2\text{O}_3$  nanostructure, the quantum yield was 28% higher than that of  $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ . This enhanced photoluminescence (PL) is attributed to a  $\text{Gd}_2\text{O}_3$  surface shell serving (i) as a sensitizer with energy transfer to the  $\text{Eu}^{3+}$  in the  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$  shell, plus (ii) passivation of non-radiative surface quenching sites. Enhanced PL was also demonstrated from polyol-synthesized  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$  nanocrystals. Increased PL can also be achieved by incorporating  $\text{Bi}^{3+}$  sensitizer ions into colloidal  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals which were self-assembled into almond-like clusters composed of ~60 nm nanorods. With 2%  $\text{Bi}^{3+}$  co-doped in  $\text{GdVO}_4:\text{Eu}^{3+}$  nanocrystals, PL was enhanced by 45%, 90% and 570% when excited by 280, 323 and 347 nm photons, respectively. This enhancement is attributed to increased absorption from Bi-O bonds, plus extension of the excitation band edge to longer wavelength. For  $\text{Bi}^{3+}$  ion concentrations  $>10\%$ , PL from co-doped nanocrystals decreased due to non-radiative decay from  $\text{Bi}^{3+}$ -induced trapping centers, as well as increased  $\text{Bi}^{3+}$ - $\text{Bi}^{3+}$  energy transfer instead of  $\text{Bi}^{3+}$ - $\text{Eu}^{3+}$  transfer.

2:20pm **AC-TuA2 Memory Effects of  $\text{UF}_6$  Adsorption and Reaction at Metallic Surfaces**, *M.T. Puffett, D.P. Moore, J.D. Farr, R.K. Schulze, K.D. Ianakiev*, Los Alamos National Laboratory

In this study we explore memory effects that arise from the reactivity of  $\text{UF}_6$  with surface hydroxyls (and other entities with a reactive H bond) that may be present at metallic surfaces. These chemical interactions are noted to leave behind low but measurable quantities of uranium oxy fluorides ( $\text{UO}_2\text{F}_2$ ,  $\text{UOF}_4$  and related extended solids). Uranium re-depositions are noted to occur following sequential exposures to varying isotopic content in the  $\text{UF}_6$  gas stream. We explore the role that additional fluorinating agents ( $\text{HF}$ ,  $\text{ClF}_3$ ) play in promoting uranium surface re-fluorination and memory effects in these deposits. The primary surface and radiochemical characterization techniques utilized in this study and include x-ray photoelectron spectroscopy, Auger electron spectroscopy depth profiling, static SIMS and alpha emission spectroscopy. The importance of these memory effects in enabling higher accuracy isotopic determinations and in forensic knowledge

2:40pm **AC-TuA3 Nanocomposites for Thermoelectrics : Erbium Mono-Antimonide Nano Crystals Embedded in Group III -AsSb Host Materials**, *T. Onishi*, University of California, Santa Cruz and NASA Ames Research Center, *T. Favaloro*, University of California, Santa Cruz, *A. Shakouri*, University of California, Santa Cruz and NASA Ames Research Center, *E. Coleman, G.S. Tompa*, Structured Materials Industries Inc., *S. Kraemer, H. Lu, A. Gossard*, University of California, Santa Barbara, *N.P. Kobayashi*, University of California, Santa Cruz and NASA Ames Research Center

The increasing demand for efficiency in energy generation and use has increased interest in thermoelectrics (the direct conversion of heat to electricity), which has the promise to increase energy efficiency – if certain cost-performance metrics are met. However, in the continuing quest of the efficient bulk thermoelectrics material for more than 50 years, the improvement of thermoelectric properties has not been sufficient to widely replace other established power sources.

One of the promising lines of new material development is based on the use of nanostructures to dramatically change the heat transport properties of thermoelectrics while largely leaving the electrical properties intact. In this effort we have focused on developing nanocomposites comprised of thin

films containing semi-metallic nanocrystals. We herein report on the growth of nanocomposites that consist of erbium monoantimonide (semi-metal) in the form of nano crystals or nanocolumns self-assembled with in thin film group III- arsenide/antimonide alloys doped with acceptors. The nano composites are optimized in terms of three factors, electrical conductivity, and thermal conductivity, and Seebeck coefficient to maximize thermoelectric figure of merit.

Using low-pressure metal organic chemical vapor deposition (MOCVD), we have developed the growth processes of the nanocomposites that consist of indium gallium (arsenic) antimonide ( $\text{InGa(As)Sb}$ ) host materials with embedded erbium antimonide (ErSb) nanocrystals. The size of ErSb nano crystals, carrier density and alloy composition of the  $\text{InGa(As)Sb}$  host materials are tuned by controlling of various growth parameters. The following techniques were used to obtain information on the growth of ErSb nanocomposites embedded  $\text{InGa(As)Sb}$  film on n-type  $\text{InSb}$  (100) substrate: Scanning Electron Microscopy (SEM), Fourier Transform Infra-Red-absorption (FTIR), Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM).

Acknowledgement:

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3:00pm **AC-TuA4 TRU Waste Disposal in Waste Isolation Pilot Plant, WIPP**, *M. Borkowski, H. Khaing, J.-F. Lucchini, D.T. Reed, M.K. Richmann, J.S. Swanson, D. Ams*, Los Alamos National Laboratory

The mobility and potential release of actinides into the accessible environment continues to be the key performance assessment concern of nuclear repositories. Actinide, in particular plutonium speciation under the wide range of conditions that can exist in the subsurface is complex and depends strongly on the coupled effects of redox conditions, inorganic/organic complexation, and the extent/nature of aggregation. Understanding the key factors that define the potential for actinide migration is, in this context, an essential and critical part of making and sustaining a licensing case for a nuclear repository. Herein we report on recent progress in a concurrent modeling and experimental study to determine the speciation of plutonium, uranium and americium in high ionic strength Na-Cl-Mg brines. This is being done as part of the ongoing recertification effort in the Waste Isolation Pilot Plant (WIPP).

A key feature of salt-based repositories is the relatively rapid self-sealing nature of the salt. This feature leads to geologic isolation of the waste form, and when reduced metals are present (e.g., iron containers), the system is driven anoxic by corrosion leading to strongly reducing environments. The consequence of this is that the combination of anaerobic microbial activity, reactions of reduced metals, and, when present, reactions of organics leads to the reduction of higher valent Pu(V) and Pu(VI) species to the lower valent Pu(III) and Pu(IV) species. The reduction of Pu(V/VI) species has been studied extensively. Less is known about microbial effects with halophiles although there is no question that bioreduction of higher valent plutonium occurs readily by soil bacteria under anoxic conditions. These lower valent oxidation states have lower solubilities and correspondingly lead to lower solubility and mobility of the plutonium.

The oxidation-state specific solubility of actinides were established in brine as function of  $\text{pC}_{\text{H}^+}$ , brine composition and the presence and absence of organic chelating agents and carbonate. An oxidation-state invariant analog approach using  $\text{Nd}^{3+}$  and  $\text{Th}^{4+}$  was used for  $\text{An}^{3+}$  and  $\text{An}^{4+}$  respectively. These results show that carbonate and hydrolysis predominate at  $\text{pC}_{\text{H}^+}$  above 8. Organic complexation is more important for  $\text{An}^{3+}$ . Carbonates are the key factor for U(VI) solubility. Modeling efforts are focused on the use of Pitzer parameters to correct for high-ionic strength effects and show that there is still some uncertainty about the predominant carbonate and hydrolytic species, particularly when longer-term timeframes are considered.

4:00pm **AC-TuA7 Elastic Moduli of Pure Alpha, Beta, Gamma Plutonium—Three Different Metals**, *A. Migliori*, Los Alamos National Laboratory

From 10 K to 580K plutonium changes phase from monoclinic alpha to body centered monoclinic beta to orthorhombic gamma structures. Each crystal structure is rare or unique for an elemental metal. Measurements presented here provide the first high-accuracy values for a single high-purity specimen of the elastic moduli of unalloyed polycrystal plutonium as a function of temperature throughout the entire range of existence of the alpha, beta, and gamma phases. The bulk and shear moduli, essential

thermodynamic material properties, reflect important and huge changes with temperature, such that these phases present as three different metals. Unlike phase transformations in many other elements where the bonding, nearest-neighbor distances, and physical properties are closely related among phases, in the three lowest-temperature phases of plutonium, the relationships are missing, and support the extreme sensitivity of plutonium properties to phase, temperature, and almost-certainly, electronic structure. We describe here the characteristics and implications of these newly-observed properties.

4:20pm **AC-TuA8 Self Diffusion Coefficients of Trivalent Element Ions in Moderately Dilute Aqueous Solutions: Comparative Study between Lanthanum and f-elements.** *H. Latrous*, Faculté des sciences de Tunis, Tunisia, *R. Besbes*, IPEST, Tunisie, Tunisia, *N. Ouerfelli*, Faculté des Sciences de Tunis, Tunisia, *A. manef*, IPEST, Tunisie, Tunisia

Our work continues our studies on the trivalent ions 4f and 5f elements. In this paper, we have summarized data relatives to measurements of self-diffusion coefficients, conductance, mobility and activity coefficients for trivalent f-elements ions. Self-diffusion coefficients,  $D_i$  of the trivalent f-elements aquo ions series have been determined in aqueous electrolyte support at 25°C using the open-end capillary method (O.E.C.M.), from concentration 0 to 1.5M. We verify its variation with concentration and ionic strength of medium.

Variation of  $D_i/D_i^\circ$  versus  $\sqrt{C}$  (C: molar concentration) for  $\text{La}^{3+}$  in acid medium pH=2.5, verify Nernst-Hartley expression. Activity coefficients  $\gamma_{\pm}$  for  $\text{LaCl}_3$  at pH = 2.5 deduct from diffusion measurements are compared with recent data measured by *f.e.m* and are discussed in term of association phenomena (ion-pairing).

4:40pm **AC-TuA9 Synthesis and Characterization of Scintillating  $\text{Gd}_2\text{SiO}_5:\text{Ce}$  Nanoparticles using Hot-Solution Growth.** *J. Choi*, *T.-K. Tseng*, *M.R. Davidson*, *P.H. Holloway*, University of Florida

Scintillation detectors are commonly used for measuring radiation from nuclear materials. To date the scintillating material has been a single crystal, commonly doped with a rare earth ion that controls the wavelength and intensity of radioluminescence. Scintillating nanoparticles have the potential to replace the expensive, energy-intensive, limited volume single crystal detectors. In this study, scintillating  $\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$  (GSO) nanoparticles with 5~10 nm diameters were prepared by a two-pot hot-solution growth (HSG at 200~300 °C) method. The Ce dopant concentration was varied between 0.2%~5% and concentration quenching was examined by photoluminescence (PL). Low (0.5% Ce) doped GSO nanoparticles exhibited good PL from both as-synthesized and calcined (1100°C for 2 h in air) nanoparticles. Concentration quenching for nanoparticles occurred at higher Ce concentrations than for bulk samples; this will be discussed. The PL emission was from the 5d to two 4f levels ( $^2T_2$  to  $^2F_{7/2}$  and  $^2F_{5/2}$  transitions) of  $\text{Ce}^{3+}$  at 420~450 nm. Photoluminescent excitation (PLE) spectra showed that the emission resulted from the direct excitation of the 4f~5d transition of  $\text{Ce}^{3+}$  excited between 270~375 nm. X-ray diffraction (XRD) and transmission electron microscopy (TEM) data showed that the GSO nanoparticles were amorphous as grown, but well crystallized after calcining. Quantum yield and radioluminescence data will be presented and discussed.

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