

**Final Project Report for ER15351**  
**“A Study of New Actinide Zintl Ion Materials”**

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### I. Introduction

During the project, annual reports have been submitted that described the work accomplished. This report will summarize those reports. During the grant period, one Ph.D. student finished his degree and transitioned to a postdoc position and was hired as a staff member at Los Alamos National Laboratory (Dr. Ryan F. Hess). Three postdocs were hired: Dr. Paula Briggs-Piccoli (University of Arizona), Dr. Benny C. Chan (Penn State University) and Dr. Hugh D. Selby (University of Arizona). Dr. Briggs-Piccoli was hired on as a staff member at Argonne National Laboratory, Dr. Chan has been teaching at The College of New Jersey, and Dr. Selby was hired on as a staff scientist at Los Alamos. Four undergraduate students at Colorado State were also trained during the project period and appear as coauthors on our papers: Ms. Sarah Wilhelms (staff scientist in Boulder, CO), Ms. Jenifer Sheaffer (graduate student at Washington State in radiochemistry), Mr. Zeric Hulvey (graduate student at Notre Dame), and Mr. Patrick Feng (graduate student at UC-San Diego). Workers at Los Alamos received considerable support from the Seaborg Institute for Transactinium Science and NMT-2 to supplement their salaries to be commensurate with comparable LANL students and postdocs.

It is important to note, during the project period, the “Alpha wing” at TA-48 had been closed due to several safety and inventory problems for a total of ~20 months. Dr. Chan was scheduled to begin work at the facility in late 2002 but was only able to spend a total of 8 weeks working at LANL. Dr. Selby began training in the facility in June 2004, but the facility was closed during the lab shutdown in July 2004, and he was not been able to work in the facility for over one year. Subsequently, Dr. Selby was called back to Colorado State to complete work on uranium and thorium chemistry. In 2006, he was able to start work on plutonium chemistry at LANL.

Despite the inaccessibility to the plutonium handling facility at Los Alamos during more than 2 years of the project, we were able to complete a number of studies on Th and U chemistry at Colorado State and several with Dr. Steve Conradson. This work resulted in 18 manuscripts that have been published. A list of those publications may be found at the end of this report. Finally, this work has been presented at 12 international invited symposia, 15 university invited presentations, 4 workshops (NSF and DOE/NSF) and 4 general public talks on actinide chemistry.

### II. Project Highlights

#### **Ternary Actinide Structures, $AU_2Se_6$ ( $A = K, Cs$ )**

A series of ternary chalcogenide ternary compounds have been reported by others, including  $KTh_2Q_6$  ( $Q = Se, Te$ ),  $CsTh_2Se_6$ , and  $CuTh_2Se_6$ . These compounds consist of layers of thorium selenide polyhedra that contain an elongated Q-Q bond, which has also been seen in

$\text{RbDy}_3\text{Se}_8$  and  $\text{CsCe}_3\text{Te}_8$ . The formal oxidation state for thorium is most likely tetravalent while the rare earth is most likely trivalent. The oxidation state for the chalcogenide atoms in these phases is difficult to assign but a model of mixed oxidation state selenium has been proposed. Our group has recently synthesized a plutonium analog,  $\text{KPu}_3\text{Se}_{8-x}$ , which is isostructural to  $\text{RbDy}_3\text{Se}_8$  but with one partially-occupied selenium site. Plutonium apparently prefers a structure where it behaves more like a rare earth element, while thorium prefers a structure more like a transition metal as found in  $\text{ZrSe}_3$ .

We have prepared the uranium analog in this series of compounds,  $\text{AU}_2\text{Se}_6$  ( $\text{A} = \text{K}, \text{Cs}$ ). The compounds are isostructural to the previously reported  $\text{KTh}_2\text{Se}_6$ . The  $[\text{U}_2\text{Se}_6]^-$  layers are similar to the  $\text{ZrSe}_3$  and  $\text{ThSe}_3$  structure types. For  $\text{AU}_2\text{Se}_6$  and the thorium analogs, the alkali metal resides within the interlayer spaces of the compound. For  $\text{KPu}_3\text{Se}_{8-x}$ , the structure is isostructural to  $\text{RbDy}_3\text{Se}_8$ . The  $[\text{Pu}_3\text{Se}_{8-x}]^-$  layer is related to  $\text{NdTe}_2$ ,  $\text{NdTe}_3$ , and  $\text{PuSe}_2$  structure types and the alkali metal resides within the interlayer spacing of the  $[\text{Pu}_3\text{Se}_{8-x}]^-$  layers. The uranium and thorium structures are related to a transition metal structure, while the plutonium analog is related to a rare earth structure, suggesting a more rare earth like chemistry for plutonium chalcogenides, Figure 1.

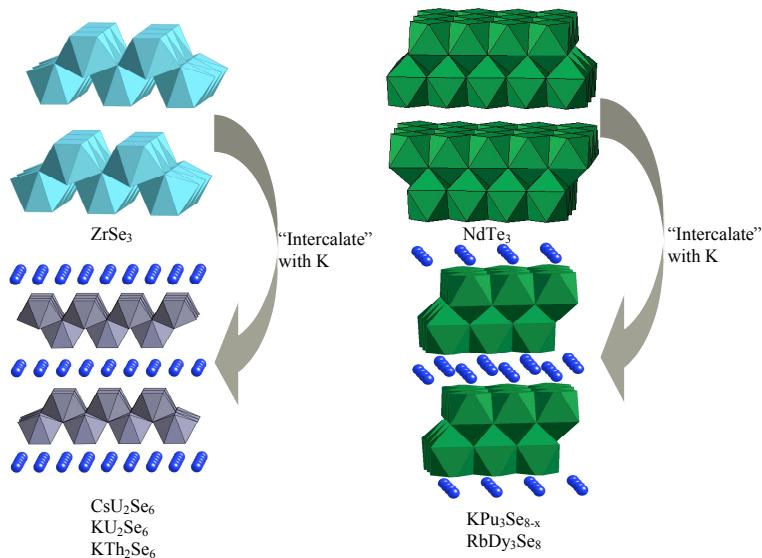


Fig. 1. The relationship between parent structures and alkali actinide selenide compounds is apparent by theoretically “intercalating” the alkali metal between the metal chalcogenide layers.

X-ray Photoelectron spectroscopy (XPS) spectra were collected for  $\text{KU}_2\text{Se}_6$  to elucidate the oxidation states of uranium and selenium. The binding energy for the  $4f7/2$  peak of uranium was at 380.5 eV. The

peak was correlated to the 380.6 eV peak of  $\text{UO}_2$  so the formal oxidation state was assigned as +4. Two distinct oxidation states were observed for the  $3d5/2$  peak of selenium at 55.3 eV and 53.4 eV. The peak at 53.4 eV was correlated to  $\text{PbSe}$ , also at 53.4 eV, so the oxidation state can be assigned as -2. The peak at 55.3 eV was correlated to  $\text{USe}$ , also at 55.3 eV.  $\text{USe}$  contains a polyselenide network of selenium that makes the oxidation state difficult to assign.

With our Quantum Design MPMS magnetometer at Colorado State University, we were able to obtain magnetic data on the uranium compounds. The  $1/\chi$  versus  $T$  plots were linear for  $\text{AU}_2\text{Se}_6$  compounds indicating the materials are paramagnetic. For  $\text{KU}_2\text{Se}_6$  the magnetic moment was calculated to be  $2.79 \mu\text{B}$ , which is consistent for the spin only contribution of  $\text{U}^{4+}$  with two unpaired electrons.

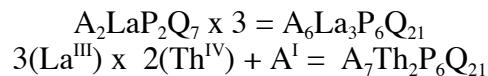
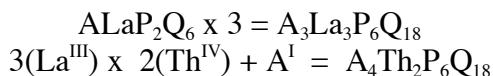
### Quaternary Actinide Chalcophosphate Structures, $\text{Cs}_4\text{Th}_2\text{P}_6\text{S}_{18}$ and $\text{Rb}_7\text{Th}_2\text{P}_6\text{Se}_{21}$

The molten alkali metal polychalcogenide flux method has produced a host of novel and complex compounds during this last and the previous project periods. Our group has explored

the actinide chalcophosphate phase space and discovered many novel compounds, including  $\alpha$ -K<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub>, Cs<sub>8</sub>U<sub>5</sub>(P<sub>3</sub>S<sub>10</sub>)<sub>2</sub>(PS<sub>4</sub>)<sub>4</sub>, K<sub>10</sub>Th<sub>3</sub>(P<sub>2</sub>S<sub>7</sub>)<sub>4</sub>(PS<sub>4</sub>)<sub>2</sub>, A<sub>5</sub>An(PS<sub>4</sub>)<sub>3</sub> (A = K, Rb, Cs; An = U, Th), K<sub>3</sub>Pu(PS<sub>4</sub>)<sub>3</sub>, and APuP<sub>2</sub>S<sub>7</sub> (A = K, Rb, Cs). Our work demonstrated the remarkable diversity of actinide containing chalcophosphate compounds and that the phase space is still ripe to discover more novel compounds.

We have discovered two new thorium chalcophosphates, Cs<sub>4</sub>Th<sub>2</sub>P<sub>6</sub>S<sub>18</sub> and Rb<sub>7</sub>Th<sub>2</sub>P<sub>6</sub>Se<sub>21</sub>, which exist as layered and one-dimensional structures, respectively. Cs<sub>4</sub>Th<sub>2</sub>P<sub>6</sub>S<sub>18</sub> crystallizes as colorless blocks in the triclinic space group  $P_{-1}$ . The structure consists of (Th<sub>2</sub>P<sub>6</sub>S<sub>18</sub>)<sup>4-</sup> layers separated by layers of cesium cations and the layers only contain the (P<sub>2</sub>S<sub>6</sub>)<sup>4-</sup> building block. Rb<sub>7</sub>Th<sub>2</sub>P<sub>6</sub>Se<sub>21</sub> crystallizes as red blocks in the triclinic space group  $P_{-1}$  (no. 2). The structure consists of linear ribbons of (Th<sub>2</sub>P<sub>6</sub>Se<sub>21</sub>)<sup>7-</sup> separated by rubidium cations and the ribbon contains both the (PSe<sub>4</sub>)<sup>3-</sup> and (P<sub>2</sub>Se<sub>6</sub>)<sup>4-</sup> building blocks. Optical band gap measurements correlated the crystal colors and their respective electronic band gaps. Solid state Raman spectroscopy of both compounds confirmed the presence of their respective chalcophosphate building blocks.

Both compounds have no known rare earth analogs; however, the empirical formulae are related to two classes of rare earth compounds, AREP<sub>2</sub>Q<sub>6</sub> (A=Na, K; RE=La, Ce, Pr, Sm, Gd; Q = S, Se) and A<sub>2</sub>REP<sub>2</sub>Q<sub>7</sub> (A = K, Rb, Cs; RE = La, Ce, Sm; Q = S, Se), by the following considerations:



If the actinide is substituted into the rare earth structure, the compound will not charge balance with the rare earth being trivalent and the actinide being tetravalent. An alkali cation is substituted into a rare earth site to form the novel actinide chalcophosphate structures, Figure 2.

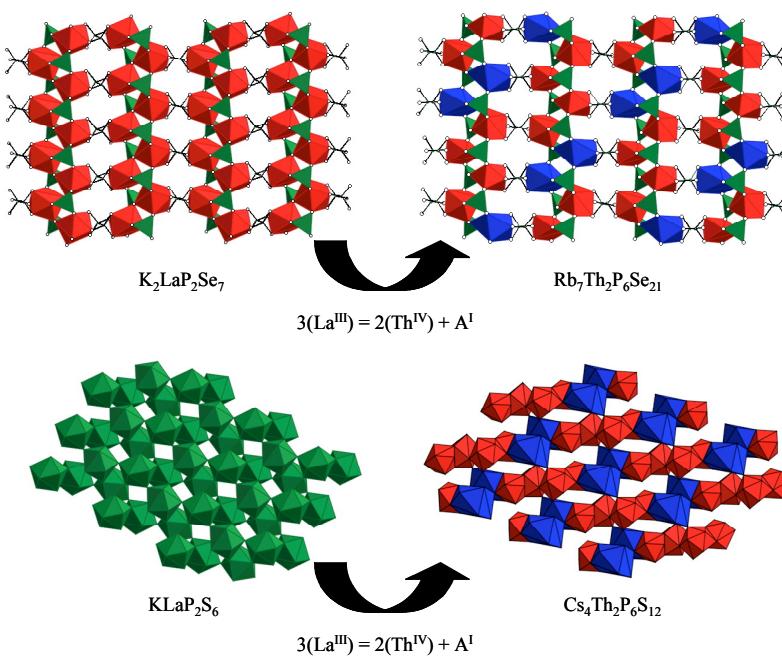


Figure 2. The relationship between the actinide and rare earth chalcophosphate is achieved by replacing 3 rare earth sites with 2 actinides and an alkali metal.

## Quaternary Actinide Thiocuprate Structures

Besides its key role in high temperature superconductors, copper is an interesting element in a number of chalcogenide-based phases. The lower chalcogenides (S-Te) can stabilize the  $\text{Cu}^+$  ion because of lower oxidizing power relative to oxygen. The soft  $d^{10}$  ion electronic nature of  $\text{Cu}^+$  allows flexible structural and coordination environments including potential  $\text{Cu}^+-\text{Cu}^+$  interaction ( $\sim 2.7$  Å). Cu(I) quaternary compounds offers a remarkable number of new complex structure types; however, no obvious systematic correlation between compounds exist. Fortunately, quaternary systems can be readily mapped and structure/property relationships can be systematically examined. We have worked to complete a study of the K/Cu/An/S (An = Th, U, Pu) quaternary systems.

Thorium containing phases are less well studied than their uranium counterparts. Our early exploration of the K/Th/Cu/S system has yielded three new semiconducting, layered phases,  $\text{KCuThS}_3$ ,  $\text{K}_2\text{Cu}_2\text{ThS}_4$ , and  $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$  (*Inorg. Chem.*) The compounds vary in their color from colorless ( $\text{KCuThS}_3$ ), red ( $\text{K}_2\text{Cu}_2\text{ThS}_4$ ), and yellow ( $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$ ), which correlate to their respective band gaps of 3.0 eV, 2.0 eV, and 2.4 eV. The band gaps are direct transitions from the narrow Cu/S valence bands to sulfur-based conduction-band states, as seen in the lanthanide and transition metal analogs.

Three new quaternary  $\text{U}^{4+}$  compounds were synthesized in a similar region of phase-space as the Th compounds described above.  $\text{KCuUS}_3$  and  $\text{K}_2\text{Cu}_2\text{US}_4$  are isostructural with  $\text{KCuThS}_3$  and  $\text{K}_2\text{Cu}_2\text{ThS}_4$ , Figures 3a, c. The third,  $\text{K}_3\text{Cu}_4\text{US}_6$ , Figure 3d, features layers of isolated  $\text{U}^{4+}$  octahedra surrounded by distorted  $\text{CuS}_4$  tetrahedra separated by  $\text{K}^+$  cations. The charge of  $\text{K}_3\text{Cu}_4\text{US}_6$  does not balance as written (assuming  $\text{Cu}^+$  and  $\text{U}^{4+}$ ), however, EDS microprobe and single crystal diffraction data support the empirical formula. Oxidation states of the metals were confirmed by XPS to be only  $\text{Cu}^+$  and  $\text{U}^{4+}$ . Charge balance is likely achieved by placing “holes” in the sulfur valence bands, making the material a likely p-type conductor. Crystallography could not distinguish differences between potential  $\text{S}^{1-}/\text{S}^{2-}$  species.

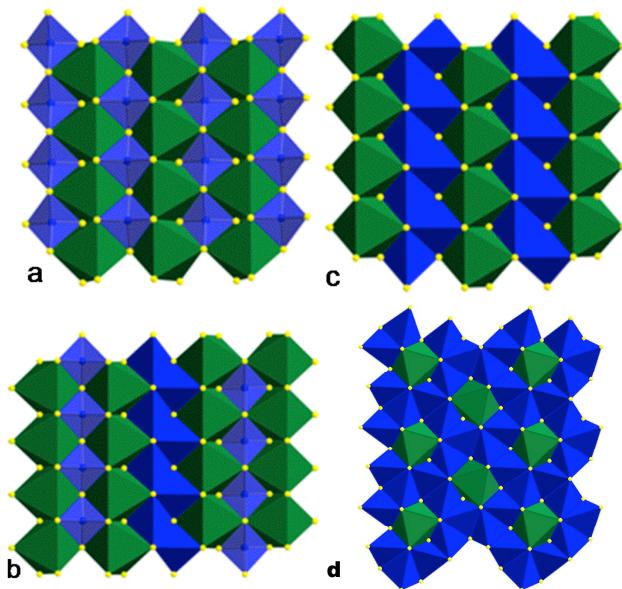


Fig. 3. The actinide chalcocuprates layers are shown, (a)  $\text{KCuAnS}_3$ , (b)  $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$ , (c)  $\text{K}_2\text{Cu}_2\text{AnS}_4$ , (d)  $\text{K}_3\text{Cu}_4\text{US}_6$ , where An = U, Th.

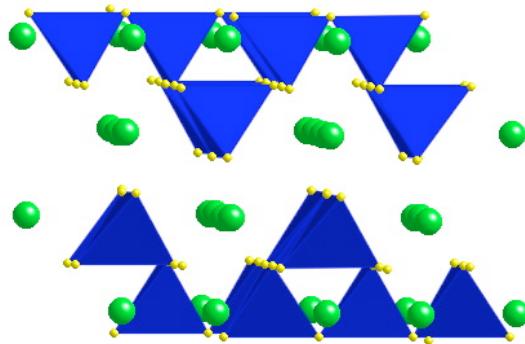
As expected, all three uranium-containing compounds display paramagnetic behavior at room temperature and are described in terms of the relative closeness of the  $\text{U}^{4+}$  octahedra. In  $\text{K}_3\text{Cu}_4\text{US}_6$ , there would be no expected coupling between uranium cations due to the separation of the uranium octahedra by the  $\text{CuS}_x$  moieties. In  $\text{K}_2\text{Cu}_2\text{US}_4$ , there are no interactions between adjacent uranium cations in the linear chains of edge-shared uranium octahedral.  $\text{KCuUS}_3$  displays an antiferromagnetic transition at  $T_n = 61$  K. In the paramagnetic region above 60 K, the compound exhibits Curie-Weiss behavior with

a Weiss constant of  $-58.4$  K indicating a net long range antiferromagnetic behavior. The magnetic moment was calculated to be  $2.61 \mu\text{B}$ , which is similar to the theoretical spin only contribution.

## Metathesis Reactions to Prepare New Materials

We attempted to prepare new and known materials with new Zintl ion salts as metathesis reaction precursors as well as using Cu/CuCl<sub>2</sub> as a reactants. We prepared and characterized 5 new ternary “starting material” compounds: K<sub>2</sub>P<sub>2</sub>Se<sub>6</sub>, K<sub>4</sub>P<sub>2</sub>Se<sub>6</sub>, K<sub>3</sub>PSe<sub>4</sub>, Cs<sub>4</sub>Si<sub>2</sub>Se<sub>8</sub>, and Cs<sub>4</sub>Si<sub>4</sub>Se<sub>10</sub> (see published work, Section III). These phases were reacted with uranium and plutonium chloride salts to demonstrate that reactions with specific tetrahedral phosphate and silicate building blocks could be preformed with actinide halide starting materials rather than the metals (all other previous reactions were run with U and Th metals). We used a halide scavenger (Tl) to try to help the reactions proceed to completion. However, in the case of Pu, a new Pu-doped thallium salt was isolated and characterized: Pu-TlCuS<sub>2</sub>, Fig. 4. While this is a known structure type, this demonstrated for the first time the ability to utilize preformed salts as reactants to with PuCl<sub>3</sub>.

Fig. 4. Pu-TlCuS<sub>2</sub>, with green Pu/Tl spheres and blue Cu tetrahedra.



## Alkali Metal Precursor Materials.

During the exploration of quaternary phase space, novel ternary structures are often discovered. In an attempt to make a selenium analog of K<sub>5</sub>Th(PS<sub>4</sub>)<sub>3</sub>, a novel ternary structure, K<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> crystallized along with KTh<sub>2</sub>Se<sub>6</sub>. K<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> consists of linear chains of ethane-like P<sub>2</sub>Se<sub>6</sub> building blocks that are connected by a Se-Se bond, Figure 5a. Raman spectroscopy showed the presence of the P<sub>2</sub>Se<sub>6</sub> building block along with a stretch consistent with a Se-Se bond. This material is particularly interesting because it represents the high pressure phase of KTbP<sub>2</sub>Se<sub>6</sub>. The rare earth material was placed under high pressures, ~9.2 Gpa, in a diamond anvil cell and underwent a phase transition accompanied by a shift in absorption edge to red and a formation of a Se-Se bond. The same absorption edge and linear chain selenophosphate structural motif are seen in both K<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> and high pressure KTbP<sub>2</sub>Se<sub>6</sub>.

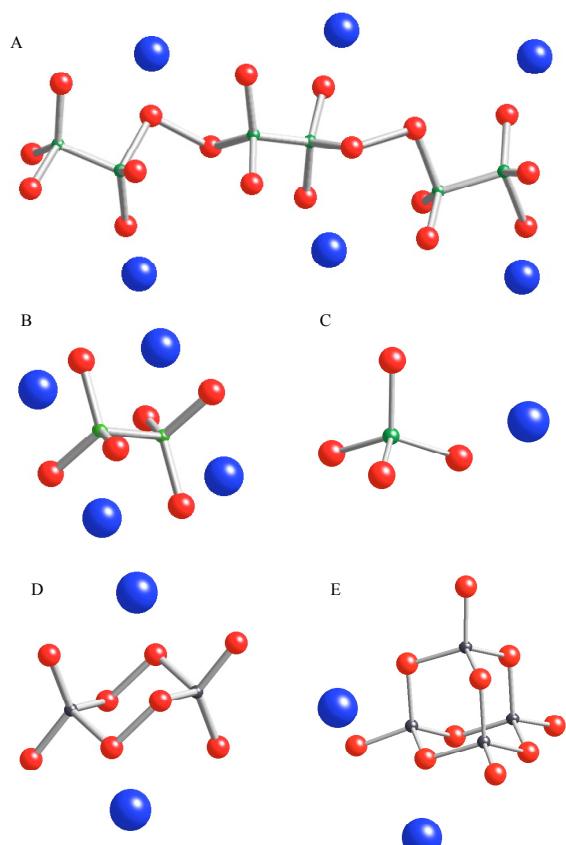


Figure 5. New ternary “starting material” compounds, (a) K<sub>2</sub>P<sub>2</sub>Se<sub>6</sub>, (b) K<sub>4</sub>P<sub>2</sub>Se<sub>6</sub>, (c) K<sub>3</sub>PSe<sub>4</sub>, (d) Cs<sub>4</sub>Si<sub>2</sub>Se<sub>8</sub>, and (e) Cs<sub>4</sub>Si<sub>4</sub>Se<sub>10</sub>. Blue spheres are the alkali metal, red spheres are selenium, green spheres are phosphorous, and gray spheres are silicon.

The ternary (K-P-Se) phase diagram was explored and  $K_2P_2Se_6$  was prepared without thorium. Two unpublished potassium selenophosphates,  $K_3PSe_4$  and  $K_4P_2Se_6$ , were discovered.  $K_3PSe_4$  consists of  $(PSe_4)^3^-$  tetrahedra surrounded by K cations, Figure 5c. The compound is isostructural to  $K_3PS_4$ .  $K_4P_2Se_6$  consists of ethane-like  $(P_2Se_6)^4^-$  units surrounded by K cations, Figure 5b. The compound is isotypic to  $Tl_4P_2Se_6$ . The phase diagram indicated that  $K_3PSe_4$  forms at the selenium rich region of phase space, where the conditions are highly oxidizing.  $K_2P_2Se_6$  and  $K_4P_2Se_6$  formed in reactions containing less selenium indicating less oxidizing conditions are required so that  $P^{4+}$  and  $Se^-$  are incorporated into the compound.  $K_4P_2Se_6$  forms the region of phase space that is higher in potassium concentration as compared to  $K_2P_2Se_6$ .

We have attempted to make a uranium analog to the rare earth chalcosilicate,  $KLaSiSe_4$ . A new ternary,  $Cs_4Si_2Se_8$ , was serendipitously discovered. The structure consists two tetrahedra of  $SiSe_4$  bound by an Se-Se bond to form a ring complex of  $(Si_2Se_8)^4^-$  surrounded by Cs cations, Figure 5d. The compound is isostructural to  $Cs_4Ge_2Se_8$ . While attempting to make  $Cs_4Si_2Se_8$  without the presence of uranium, we also discovered  $Cs_4Si_4Se_{10}$ , which crystallizes with adamantine-like  $[Si_4Se_{10}]^{4-}$  units composed of four corner shared  $SiSe_4$  units and Cs cations charge balancing the compound, Figure 5e. The compound is isostructural with  $Cs_4Ge_4S_{10}$ . These new ternary compounds will be used as “starting materials” for a series of metathesis reactions that we hope will result in several new target phases that may be explored by other groups in future years.

### III. Manuscripts Resulting from ER 15351

P. M. Briggs-Piccoli, K. D. Abney, J. R. Schoonover, P. K. Dorhout "Synthesis and Structural Characterization of Quaternary Thorium Selenophosphates:  $A_2ThP_3Se_9$  ( $A = K, Rb$ ) and  $Cs_4Th_2P_5Se_{17}$ " *Inorg. Chem.*, **2000**, *39*, 2970-2976.

P. M. Briggs Piccoli, K. D. Abney, J. R. Schoonover and P. K. Dorhout. "Synthesis, Structure and Properties of  $Cs_4Th_4P_4Se_{26}$ : a Quaternary Thorium Selenophosphate Containing the Unique  $(P_2Se_9)^6^-$  Anion." *Inorg. Chem.* **2001**, *40*, 4871-4875.

R. F. Hess, K. D. Abney, J. M. Burris, H. D. Hochheimer, P. K. Dorhout "Synthesis and Characterization of Six New Quaternary Actinide Thiophosphate Compounds  $Cs_8U_5(P_3S_{10})_2(PS_4)_6$ ,  $K_{10}Th_3(P_2S_7)_4(PS_4)_2$ , and  $A_5An(PS_4)_3$ , ( $A = K, Rb, Cs$ ;  $An = U, Th$ )."  
*Inorg. Chem.* **2001**, *40*, 2851-2859.

R. F. Hess, P. L. Gordon, C. D. Tait, K. D. Abney, P. K. Dorhout "Synthesis and Characterization of The First Quaternary Plutonium Thiophosphates:  $K_3Pu(PS_4)_2$  and  $APuP_2S_7$ , ( $A = K, Rb, Cs$ )" *J. Am. Chem. Soc.* **2002**, *124*, 1327-1333.

P. M. Briggs-Piccoli, K. D. Abney, P. K. Dorhout, "The Synthesis and Structural Characterization of a New Beta Phase of  $K_2ThP_3Se_9$ " *J. Nuc. Sci. Tech.* **2002**, *3*, 611-615.

A. J. Lupinetti, J. L. Fife, E. Garcia, P. K. Dorhout, K. D. Abney, "Low-Temperature Synthesis of Uranium Tetraboride by Solid-State Metathesis Reactions" *Inorg. Chem.* **2002**, *41*, 2316-2318.

S. D. Conradson, K. D. Abney, B. D. Begg, E. D. Brady, D. L. Clark, C. den Auwer, M. Ding, P. K. Dorhout, F. J. Espinosa-Faller, P. L. Gordon, N. J. Hess, R. F. Hess, D. W. Keogh, G. H. Lander, A. J. Lupinetti, L. A. Morales, M. P. Neu, P. D. Palmer, P. Paviet-Hartmann, S. D. Reilly, W. H. Runde, C. D. Tait, D. K. Veirs, F. Wastin, "High Order Speciation Effects on Plutonium L3 X-ray Absorption Near Edge Spectra", *Inorg. Chem.* **2004**, *43*, 116-131.

S. D. Conradson, B. D. Begg, D. L. Clark, C. den Auwer, M. Ding, P. K. Dorhout, F. J. Espinosa-Faller, P. L. Gordon, R. G. Haire, N. J. Hess, R. F. Hess, D. W. Keogh, L. A. Morales, M. P. Neu, P. Paviet-Hartmann, W. Runde, C. D. Tait, D. K. Veirs, P. M. Villella "Local and Nanoscale Structure and Speciation in the  $\text{PuO}_{2+x-y}(\text{OH})_{2y} \bullet z\text{H}_2\text{O}$  System" *J. Am. Chem. Soc.* **2004**, *126*, 13443-13458.

B. C. Chan, R. F. Hess, P. L. Feng, K. D. Abney, P. K. Dorhout "Synthesis and Characterization of Two New Quaternary Thorium Chalcophosphates:  $\text{Cs}_4\text{Th}_2(\text{P}_2\text{S}_6)_3$  and  $\text{Rb}_7\text{Th}_2(\text{PSe}_4)_3(\text{P}_2\text{Se}_6)_{1.5}$ ." *Inorg. Chem.* **2005**, *44*, 2106-2113.

B. C. Chan, P. L. Feng, Z. Hulvey, L. Polyakova, R. F. Hess, K. D. Abney, P. K. Dorhout "Crystal Structure of Tetracesium Octaselenidodisilicate,  $\text{Cs}_4\text{Si}_2\text{Se}_8$ " *Z. Krist.* **2005**, *220*, 12.

P. L. Feng, B. C. Chan, P. K. Dorhout "Crystal Structure of Tetracesium Decaselenidotetrasilciate  $\text{Cs}_4\text{Si}_4\text{Se}_{10}$ " *Z. Krist.* **2005**, *220*, 13-14.

B. C. Chan, P. L. Feng, Z. Hulvey, P. K. Dorhout "Crystal Structure of Tetrapotassium Hexaselenidohypodiphosphate,  $\text{K}_4\text{P}_2\text{Se}_6$ " *Z. Krist.* **2005**, *220*, 9-10.

B. C. Chan, P. L. Feng, Z. Hulvey, P. K. Dorhout "Crystal Structure of Tripotassium Tetraselenidophosphate,  $\text{K}_3\text{PSe}_4$ " *Z. Krist.* **2005**, *220*, 11.

B. C. Chan, P. L. Feng, P. K. Dorhout "Crystall Structures of Potassium Terbium(III) Tetrasulfidogermanate,  $\text{KTbGeSe}_4$  and Potassium Praseodymium(III) Tetraselenogermanate,  $\text{KPrGeSe}_4$  and" *Z. Krist.* **2005**, *220*, 7-8.

H. D. Selby, B. C. Chan, R. F. Hess, K. D. Abney, P. K. Dorhout "Three New Phases in the K/Cu/Th/S System:  $\text{KCuThS}_3$ ,  $\text{K}_2\text{Cu}_2\text{ThS}_4$ , and  $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$ " *Inorg. Chem.* **2005**, *44*, 6463-6469.

A. K. Gray, J. M. Knaust, B. C. Chan, L. A. Polyakova, and P. K. Dorhout "Crystal structure of potassium ytterbium(III) tetrathiosilicate(IV),  $\text{KYbSiS}_4$ " *Z. Krist.* **2005**, *220*, 293.

S. D. Conradson, B. D. Begg, D. L. Clark, C. den Auwer, M. Ding, P. K. Dorhout, F. J. Espinosa-Faller, P. L. Gordon, R. G. Haire, N. J. Hess, R. F. Hess, D. W. Keogh, G. H. Lander, D. Manara, L. A. Morales, M. P. Neu, P. Paviet-Hartmann, J. Rebizant, V. V. Rondinella, W. Runde, C. D. Tait, D. K. Veirs, P. M. Villella, F. Wastin "Charge

distribution and local structure and speciation in the  $\text{UO}_{2+x}$  and  $\text{PuO}_{2+x}$  binary oxides for  $x \geq 0.25$ ” *J. Solid State Chem.* **2005**, 178, 521-535.

H. D. Selby, B. C. Chan, J. D. Thompson, E. P. Luther, K. D. Abney, P. K. Dorhout “Synthesis and Characterization of a New Family of U-Based Quaternary Phases in the K/Cu/U/S System,” in preparation for *Inorg. Chem.*