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FINAL REPORT
U.S. Department of Energy
Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

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1.0 Executive Summary:

The end of the Cold War raised the need for the technical community to be concerned with the disposition of surplus nuclear weapon material. The United States Department of Energy has determined that surplus weapons plutonium belonging to the United States will be either burned as a mixed-oxide fuel (MOX) or incorporated into a ceramic material and then placed in a geologic repository. (US DOE ROD 2000) The form of that ceramic material is a solid solution between four end member phases; $CaHfTi_2O_7$, $CaUTi_2O_7$, $CaPuTi_2O_7$, and $Gd_2Ti_2O_7$. (Ebbinghaus 2000, see Appendix A). The stability and behavior of plutonium in the proposed ceramic end member materials has only begun to be understood. Our studies into the fundamental thermodynamics of actinide substitution into these phases have begun to provide a basis for technically sound solutions to the issue of a safe, secure, and environmentally acceptable waste material. Our work has found thermodynamic trends that are beginning to be illuminated which can assist in better understanding the chemistry and phase equilibria of actinide substitution into the proposed immobilization matrix.

High temperature oxide melt solution calorimetry, one of the most powerful techniques and sometimes the only technique for providing the fundamental thermodynamic data (enthalpies) needed to extend our understanding of the phase relationships, fabrication parameters, and predictability of the proposed ceramic waste form, has been used. When combined with low temperature heat capacity measurements (yielding entropies and heat capacities), solution calorimetry provides

a full understanding of the energetics of formation (e.g., enthalpy, entropy, and Gibbs free energy) of these materials and allows the accurate modeling of the phase relationships, chemical durability, and fabrication parameters needed to optimize their compositions. The purpose of this EMSP project was to experimentally determine the enthalpy, entropy, and Gibbs free energies of formation of phases that are key to the disposition matrix (Ebbinghaus 2000, see Appendix A) of surplus weapons plutonium and its potential decomposition products.

Collaboration in this project was three fold. Samples were synthesized at Lawrence Livermore National Laboratory, LLNL, (Ebbinghaus) and at the University of California, Davis, UCD, (Navrotsky and Putnam) with supplemental synthesis efforts on zircon, $AnSiO_4$ (where An = Pu, U, and Zr) performed at Los Alamos National Laboratory, LANL, (Williamson and Huang). Solution calorimetry on successfully synthesized samples was performed at UCD (Navrotsky and Putnam) on non-radioactive materials and those materials containing uranium and thorium. A high-temperature solution calorimeter similar to those used at UCD but capable of use with actinide-containing materials was installed at Los Alamos National Laboratory, LANL, (Williamson and Putnam). Prior to the end of project funding, plutonium-containing samples had not been successfully synthesized or sufficiently characterized to determine that they were in a sufficiently phase-pure form to be examined on the solution calorimeter at LANL. However recently a sample of Pu-pyrochlore, $CaPuTi_2O_7$, has been successfully synthesized by Ebbinghaus at LLNL.

External collaboration at Brigham Young University, BYU, under non-EMSP funds (LLNL – Ebbinghaus) was initiated by Putnam and Navrotsky to determine the

heat capacities and entropies of several of the phases examined. This fruitful collaboration has extended the usefulness and value of this study considerably and is especially noteworthy.

In summary, this three-year project has yielded 90 measured and derived thermodynamic quantities with an additional 30 estimated quantities representing information on a total of 27 different mineral phases where no data existed prior to our study. To date, two graduate degrees have been (Ph.D. Putnam 1999) or will soon be awarded (Ph.D. Helean 2001) with 10 peer reviewed papers in print (see Table 4), three additional papers in press or undergoing peer review (Table 4 and appendix B), at least five other papers in preparation, and over 25 invited lectures, abstracts, and / or presentations have been given at national and international scientific meetings based on work from this project.

2.0 Research Objectives and findings

In September 2000, the U.S. and Russia reached an agreement to jointly disposition roughly 68 metric tons of weapons usable plutonium. (Agreement 2000) In Russia, 34 metric tonnes of weapons-grade plutonium will be dispositioned by burning the plutonium as mixed oxide (MOX) fuel. In the U.S., 25 metric tons of plutonium recovered from pits and clean metal will likewise be dispositioned by burning as mixed oxide (MOX) fuel and about 9 metric tonnes of plutonium stored throughout the DOE complex will be dispositioned by immobilization in a ceramic which will then be encapsulated in high-level waste (HLW) glass. In all cases, the plutonium will be made equal to or less attractive for reuse in nuclear weapons than the much larger and growing inventory of plutonium in spent nuclear fuel. This threshold of unattractiveness is commonly referred to as the "spent fuel standard." In the U.S., the final products from plutonium disposition, irradiated fuel and ceramic encapsulated HLW, will be emplaced in the Federal Waste Repository, which is assumed to be Yucca Mountain.

The ceramic form selected for the disposition of plutonium is composed of a series of titanate- based phases which are generally referred to as SYNROC (short for Synthetic Rock). The particular formulation that was selected is composed of about 80 vol % pyrochlore, about 15 vol % brannerite, and about 5 vol % rutile. If impurities are present in the PuO_2 feed material, about a half a dozen other phases can also form. The most common of these are zirconolite and a silicate glass. A screening process conducted in 1995, resulted in the selection of borosilicate glasses and titanate-based ceramics (*e.g.* SYNROCs) as the best available options for immobilization of plutonium. In 1998, a pyrochlore-rich ceramic form was selected in preference to a boro-silicate glass form. More information about the development and selection of the ceramic formulation can be found in the Plutonium Immobilization Program's Baseline Formulation report. (Ebbinghaus 2000)

Although the pyrochlore-rich ceramic is the most current application for titanate-based ceramics, the concept of SYNROC has been around for some time. The idea was first proposed by Ringwood in 1978. (Ringwood 1978) The strategy of SYNROC is to immobilize the radioactive isotopes of HLW in a mixture of minerals that all have analogs in nature that

- have survived for periods exceeding 20 million years in a wide variety of geochemical environments
- have crystal chemical properties that allow them to accept a wide range of elements into their crystalline matrix
- are thermodynamically stable together

A wide range of minerals meet these three criteria. Titanate-rich minerals were selected by Ringwood because they not only meet the above criteria, but are based on one of the most insoluble oxides known, namely TiO_2. A wide variety of different SYNROC formulations have been proposed for different HLW and actinide feed materials. These formulations and the processes used to make them are

summarized in **Table 1**. For immobilization of HLW, SYNROC-C has received the most study.

Table 1. Summary of SYNROC and related variants

Form Name	Mineralogy*	"Waste" Loading	Fabrication Process
SYNROC-A	40% Ba-feldspar, 30% hollandite, 20% perovskite, 10% zirconia, kalsilite, and/or leucite	10% HLW	Melting and Crystallizing 1330ºC
SYNROC-B	40% hollandite, 35% zirconolite, 25% perovskite,	None	Hot Pressing 1200-1400ºC
SYNROC-C	33% hollandite, 28% zirconolite, 19% perovskite, 15% rutile, 5% noble metal alloy	20% HLW	Hot Pressing 1150ºC
SYNROC-D	46% spinel solid solution, 19% zirconolite, 17% nepheline, 15% perovskite, 3% hollandite	63% HLW sludge	Hot Pressing 1050-1100ºC
SYNROC-E	79% rutile, 7% zirconolite, 7% perovskite, 5% hollandite, 2% pyrochlore	7% HLW	Hot Pressing 1300ºC
SYNROC-F	90% pyrochlore, 5% hollandite, 5% rutile	50% U-rich HLW	Hot Pressing 1250ºC
SYNROC-FA	89% pyrochlore, 8% perovskite, 3% uraninite	50% U-rich HLW	Cold Pressing and Sintering 1250-1400ºC
Mixed Waste Ceramic	36% nepheline, 31% spinel solid solution, 12% zirconolite, 12% perovskite, 5% rutile, 4% whitlockite	40% residue	Cold Pressing and Sintering 1150-1200ºC
Pu Ceramic Zirconolite-rich	80% zirconolite (with some pyrochlore), 10% hollandite, 10% rutile, < 1% PuO_2	12% Pu	Cold Pressing and Sintering 1325-1400ºC
Pu Ceramic Pyrochlore-rich	85% pyrochlore, 10% brannerite, 5% rutile, < 1% uraninite solid solution	10% Pu and 21% U	Cold Pressing and Sintering 1275-1400ºC

*All percents are given in weight percent.

Most of this SYNROC work including a pilot scale demonstration has been conducted at the Australian Nuclear Science and Technology Organization (ANSTO). For the immobilization of actinides, namely plutonium, the pyrochlore-rich ceramic has received the most study. Most of this work has been conducted in the Plutonium Immobilization Program (PIP). This is a multi-site effort including a number of DOE laboratories (ANL, LLNL, PNNL, and WSRC) and related contract work with universities (BYU and UCD) and foreign laboratories (ANSTO)

For all of the minerals listed in **Table 1**, it is important that the radioactive materials are effectively retained and it is important that the relative stability of the minerals are understood. In the case of SYNROC-C, the primary minerals of interest are zirconolite, hollandite, and perovskite. In the case of the pyrochlore-rich ceramic, the primary minerals of interest are pyrochlore, brannerite, and rutile.

In addition to the pyrochlore-rich ceramic, a number of other mineral phases have been proposed for the immobilization of plutonium and other actinides. These have all received some degree of recognition and study. These mineral phases

include zircon (Webber 1996 and Burakov 1996), zirconia (Degueldre 1996), and monazite (Boatner 1988) which was originally proposed for the immobilization of HLW. More recently zirconate-based pyrochlores (Wang 1999 and Sickafus 2000) have been proposed. All of these immobilization forms have the capability to incorporate significant amounts of plutonium and neutron absorbers for criticality safety and offer high durability in geologic environments. Therefore, they are also of interest in this thermodynamic study.

In order for the radioactive constituents to be effectively retained, the constituent mineral phases in the immobilization form must be resistant to dissolution in aqueous environments. Dissolution is related at least in part to solubility, which can be determined from a knowledge of the thermodynamics of the aqueous species and solid phases. The solubility in a complex system is usually calculated with the assistance of a free energy minimization program such as EQ3/6 and the accuracy is only as good as the data that are used. Thermodynamics for most of the solid phases of interest were not available and in most cases have since been determined by this work and related work in the Plutonium Immobilization Program.

It is also valuable to understand the relative stability of the constituent phases so that processing conditions are designed in a way that the desired phases are always obtained. The relative stability of the constituent phases are given by the thermodynamics of the solid phases under the conditions of fabrication. Again, these thermodynamics were not available and have since been determined by this work and related work in the Plutonium Immobilization Program. As an example, **Figure 1** shows the relevant phase equilibria in the pyrochlore-rich ceramic, the diagram was determined from quantitative EDS analyses at ANSTO (A in the legend) and by electron microprobe analyses at LLNL (L in the legend). In this representation, UO_2, PuO_2, and $GdO_{1.5}$ are considered as a single component and plotted on the same axis. TiO_2 is excluded from the plot since all compositions are in equilibrium with rutile and its activity is therefore fixed at unity. A considerable amount of work has been conducted in the Plutonium Immobilization Program on how the stability of the phases in **Figure 1** are affected by changes in the base composition, plutonium oxide feed impurities, and processing conditions. (Ebbinghaus 2000) Ultimately, these changes are determined by the thermodynamic stability of the individual phases, which is the subject of this work.

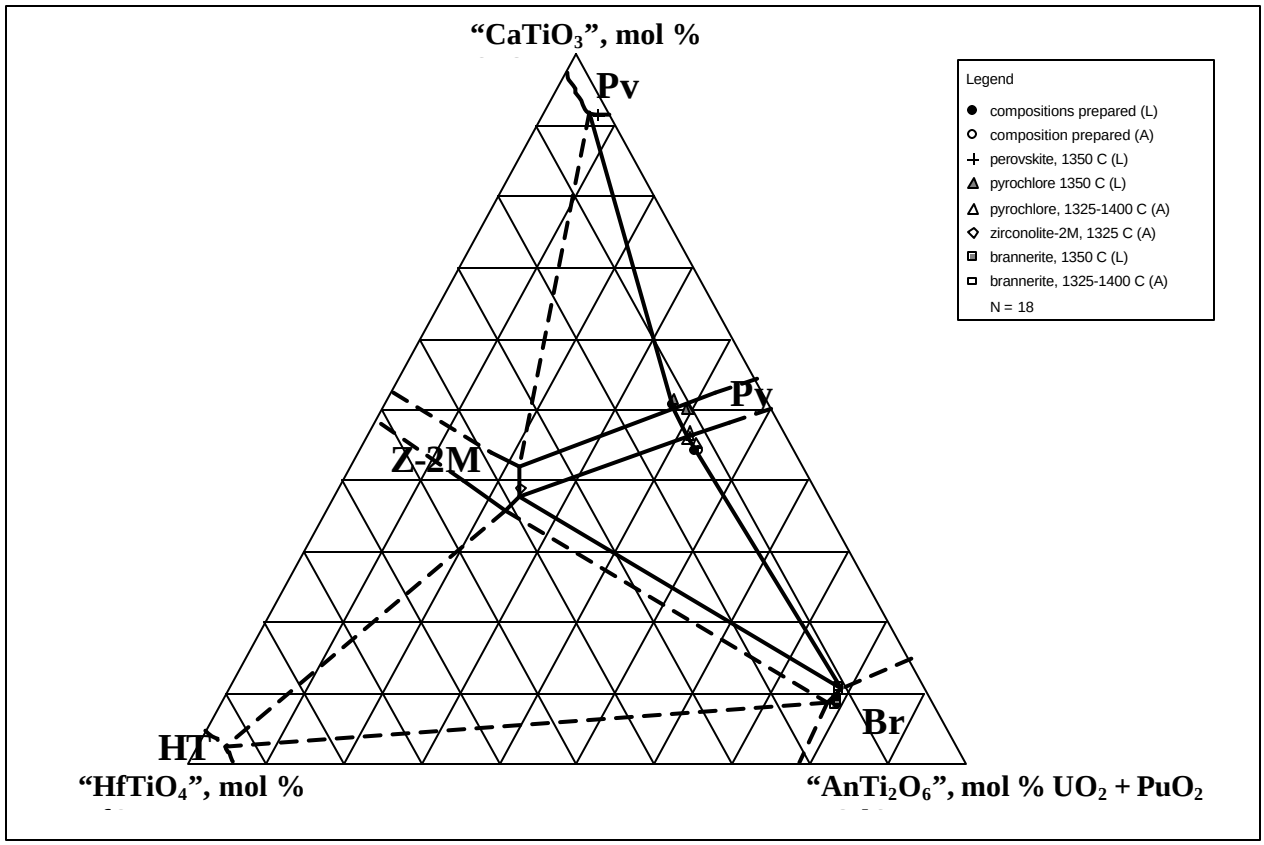


Figure 1. **$CaTiO_3$-$HfTiO_4$-$AnTi_2O_6$ phase diagram at 1350ºC in air. An = U + Pu + Gd. B = brannerite, HT = hafnium titanate, Py = pyrochlore, Pv = perovskite, Z-2M = zirocnolote-2M**

In this work, the enthalpy of formation of the end-member phases of interest has been determined. These include end-members compositions of zirconolite, pyrochlore, brannerite, hafnium titanate, perovskite, zircon, and monazite. Related heat capacity work conducted at BYU and supported by the PIP allows one to determine the remaining thermodynamic parameters for many of these end-member.

Most immediately, the thermodynamic provided by this work data will be used by the Plutonium Immobilization Program. The data is likely to be provided to DOE-RW as part of a supplemental input for the licensing application for the Federal Waste Repository. If used in their analyses, the data will be added to their thermodynamic equilibrium codes, namely EQ3/6. The data will also be used by the PIP to better understand stability of the mineral phases during sample fabrication. In this application, the thermodynamic data will be added to a suitable free energy minimization program such as the FACT program and the phase equilibria will be calculated as a function of the composition, atmosphere, and processing temperature. Ultimately, it is hoped that these data will be incorporated into the standard databases for all the commonly used free energy minimization programs, EQ3/6, FACT, Thermocalc, HSC, and MTData to name a few. Although the PIP has

the most immediate use of these data, similar ceramic forms continue to be proposed and developed for which the data obtained in this work will continue to be of value.

3.0 Calorimetric Methodology

3.1 Calorimeters

High-temperature reaction calorimetry refers to the measurement of heats of chemical reactions at temperatures above 400°C. The reactions may be of direct interest (e.g., the melting of a silicate), the oxidation of a manganese oxide, the dehydration of a zeolite, or they may represent steps in a thermodynamic cycle needed to obtain the enthalpy of interest (e.g., enthalpy of solution in molten solvent to obtain the enthalpy of formation or phase transition). The latter approach, called high temperature oxide melt solution calorimetry, has been used widely (see Navrotsky 1977,1997 for reviews). The advantages of calorimetry at high temperature generally lie in rapid and reproducible reactions of refractory materials.

The solution calorimeters used are of several types, but most have several features in common. They generally measure heat flow between a sample and heat sink maintained at an essentially constant temperature; thus they are of the isoperibol type. They are generally of the twinned variety, with two sample chambers, each surrounded by a Pt-PtRh thermopile linking it to a constant temperature metallic block. The thermopiles are linked in series opposition, and the twinned design both increases productivity and, more importantly, helps minimize the deleterious effects of small drifts in furnace and/or ambient temperature. Though no radical changes in calorimeter design have been made over the past twenty years, a number of incremental improvements have accumulated to improve the signal stability, the so called baseline, to increase the sensitivity by about a factor of seven. These improvements make routine the measurement of heat effects as small as 0.5 joule, and the use of 5-15 mg samples of silicates for solution calorimetry, in contrast with the 30-50 mg samples used in the late 1970's.

Adiabatic calorimeters are used to measure the constant pressure heat capacities (C_p) of solids. The sample and sample holder (the calorimeter) are surrounded by thermal shields maintained at the same temperature as the sample. Unlike a reaction calorimeter, it is necessary that an adiabatic calorimeter cover a wide temperature range (from below 20 K to at least room temperature) in order to calculate third-law entropies from the heat capacity data using the relation $S_m^o = \int_0^T C_p / T \, dT$. Enthalpy increments are also calculated from temperature dependent heat capacity data ($\Delta_0^T H_m^o = \int_0^T C_p dT$) which, when combined with absolute entropies and formation enthalpies measured using reaction calorimeters, can give the temperature dependence of the Gibbs free energy of formation for a particular material.

The adiabatic calorimeter at BYU is only one of two or three such instruments currently operational in the U.S. This apparatus has a demonstrated temperature range from 5 K to 400 K with an accuracy within ±0.1% and a resolution better than 0.1%. Sample sizes are generally on the order of 10 g. Although the high-temperature limit of the adiabatic calorimeter is 400 K, it has clearly been shown (Woodfield 1999) that it is possible to extrapolate the heat capacity data to high-temperatures with reasonable accuracy for these waste ceramics.

3.2 Types of Experiments

Table 2 summarizes the types of experiments that can be done in a high temperature reaction calorimeter. A transposed temperature drop experiment consists of dropping a sample from room temperature into the hot calorimeter with no solvent present. If no phase change or chemical reaction occurs, the heat content, $H_{cal\ temp}$ - $H_{room\ temp}$, is measured. Its temperature derivative gives heat capacity. If a phase transition, solid-solid or solid-liquid, takes place, the enthalpy of that change is included in the measurement. Measurements at several different calorimeter temperatures map out the heat capacity and enthalpy of transition.

Table 2. High Temperature Calorimetric Experiments

Calorimeter is essentially isothermal

Solvent present

- Solution calorimetry: sample equilibrated in hot calorimeter, then dissolved. Differences in heats of solution give heat of reaction at calorimeter T.
- Drop solution calorimetry: sample dropped from room T. Sample may be encapsulated in Au or Pt, pyrex or silica glass (which dissolves) or lead borate glass (same as solvent), or as unencapsulated pellets. Differences in heats of drop-solution give heat of reaction at room T.

Solvent absent

- Transposed temperature drop calorimetry. No permanent changes in sample: heat content measurement, includes heat of any rapid and reversible phase change.
    - o Sample changes oxidation state: difference between first and second drop related to heat of redox reaction.
    - o Sample loses H_2O, CO_2 or other volatiles: difference related to heat of devolatization.
    - o Sample undergoes irreversible phase change: difference gives heats transformation at room T.
    - o Sample undergoes change in degree of order or other structural parameters: difference gives ordering energy.

If the sample undergoes an irreversible chemical change (e.g., annealing, decomposition, dehydration, or oxidation reduction) upon dropping, the heat effect associated with that process is included in the measurement the first time the sample is dropped. An example of such an application is the study of radiation damage in zircon (Ellsworth 1994).

Dropping the sample into a solvent is called drop-solution calorimetry. It measures the heat content of the sample plus its enthalpy of solution at the

calorimetric temperature. The difference in enthalpy of drop solution of reactants and products gives the enthalpy of transformation at room temperature.

In solution calorimetry, the sample is equilibrated in the calorimeter for several hours before being stirred into the solvent and dissolved. The difference in enthalpy of solution of reactants and products yields the enthalpy of the reaction at the calorimetric temperature.

If the sample persists at calorimetric temperature, then all three types of experiments can be done. Since the enthalpy of drop solution is the sum of heat content and heat of solution, confirming this equality experimentally is a powerful indication that the calorimeter calibration factors are correct for each type of experiment, that the dissolution reactions go to completion, and that no unsuspected decomposition reactions are occurring.

4.0 Summary of Project Results

Table 3 contains an excerpt from Putnam et al. (Putnam 2001) which published a partial thermodynamic database for use in examining the stability, performance, and reliability of many of the proposed waste maticies for surplus weapon's plutonium. **Table 4** lists the completed manuscripts that have resulted from this work. In some cases the manuscripts have not completed the peer review process. In these cases we include the full, as submitted, manuscripts in **appendix B**. **Table 5** contains a listing of individuals at each institution that were supported by or contributed to this project.

4.1 Thermodynamic Quantities

Table 3. Key thermodynamic quantities obtained in this study.

Fundamental standard molar thermodynamic functions valid at 298.15 K. Units are found in the table headings. The standard state pressure is 1 atm (101 325 Pa). Errors are reported in parenthesis () applicable notes are reported in braces {} (e.g., {ac} represents the application of notes a and c). Reported for each compound are: the molar mass (Mw), the molar volume (V^o), the standard molar entropy (S^o), the standard molar enthalpy ($\Delta_f H^o$), the standard molar Gibbs free energy ($\Delta_f G^o$), and the enthalpies of reactions 1 ($\Delta_r H^o(1)$) and 2 ($\Delta_r H^o(2)$) which are: 1) the enthalpies of compound formation from the binary oxides and 2) the from the binary oxides plus perovskite, $CaTiO_3$, respectively. Data obtained in our current EMSP is **boldfaced** and estimated values are *italicized*. Literature values are referenced in Putnam 2001.

Compound name [phase, allotrope]	**Mw** $g \cdot mol^{-1}$	V^o $cm^3 \cdot mol^{-1}$	S^o $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H^o_1$ $kJ \cdot mol^{-1}$	$\Delta_f G^o_1$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(1)$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(2)$ $kJ \cdot mol^{-1}$
Zirconolite / Pyrochlore							
$CaZrTi_2O_7$ [cr]	337.0558 {a}	76.00 {b}	**193.3 (0.38)**	**-3713.7 (4.5)**	**-3514.5 (4.5)**	**-88.79 (4)**	**-8.1 (4.6)**
$CaHfTi_2O_7$ [cr]	424.3258 {a}	76.48 {b}	**194.4 (0.38)**	**-3752.2 (4.9)**	**-552.03 (4.9)**	**-111.5 (4.4)**	**-29.9 (5.3) {b}**
$CaCeTi_2O_7$ [cr]	385.9558 {a}	79.63 {b}	{c}	**-3666.5 (6.3)**	{c}	**-54.7 (5.5) {b}**	**+26.9 (6.3) {bd}**
$CaPuTi_2O_7$ [cr]	484.888 {a}	78.11 {b}		***-3636 (6) {e}***		***-56.9 (5.6) {e}***	***+25 (6) {de}***
$CaUTi_2O_7$ [cr]	483.8647 {a}	79.34 {b}		***-3653 (9) {e}***		***-44.9 (9.4) {e}***	***+36.8 (9.8) {de}***
$CaThTi_2O_7$ [cr]	477.8739 {a}			***-3782 (9) {e}***		***-32.1 (9.6) {e}***	***+49 (10) {de}***
$Gd_2Ti_2O_7$ [cr]	520.2558 {a}	80.01 {b}	{c}	**-3820.9 (4.7) {b}**	{c}	**-113.3 (2.7)**	
Brannerite							
$CeTi_2O_6$ [cr]	329.8764 {a}	67.263 {b}	***174.7 (4.8) {bf}***	**-2958.4 (5.1) {b}**	***-2787.0 (5.5) {bf}***	**+18.3 (4.7) {d}**	
$ThTi_2O_6$ [cr]	421.7945 {a}	69.348 {b}	***168.5 (4.7) {bf}***	**-3111 (6) {b}**	***-2943.9 (6.1) {bf}***	**+3.4 (4.6) {10d}**	
$PuTi_2O_6$ [cr]	428.8086 {a}	66.155 {b}	***196.9 (20.1) {bf}***	***-2896. (20.1) {b}***	***-2736.6 (20.) {bf}***	**+48 (20) {de}**	
UTi_2O_6 [cr]	427.7853 {a}	67.249 {b}	***174.4 (4.3) {bcf}***	**-2979.2 (4.5) {b}**	***-2809.4 (4.5) {bf}***	**-6.1 (4.1)**	
Zircon							

Compound name [phase, allotrope]	**Mw** $g \cdot mol^{-1}$	V^o $cm^3 \cdot mol^{-1}$	S^o $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H^o$ $kJ \cdot mol^{-1}$	$\Delta_f G^o$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(1)$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(2)$ $kJ \cdot mol^{-1}$
$ZrSiO_4$ [cr]	183.3031 {a}	39.26 {b}	84.0 (1.3)	-2034.2 (3.1)	-1919.7 (3.1)	-22.9 (3.6) {b}	
$HfSiO_4$ [cr]	270.5731 {a}	38.79 {b}			*-1973.36 {gh}*		
$CeSiO_4$ [cr]	232.2031 {a}				*-1874.59 {ghi}*		
$PuSiO_4$ [cr]	331.1353 {a}	44.66 {b}			*-1854.37 {ghj}*		
$USiO_4$ [cr]	330.112 {a}	45.84 {b}	118 (12)	-1991.3 (5.4)	-1883.6 (4.0)	+4.4 (5.5) {b}	
$ThSiO_4$ [cr]	324.1212 {a}	48.41 {b}			*-2050.1 (4.3)*		
$AmSiO_4$ [cr]	335.0831 {a}				*-1764.77 {gh}*		
Monazite							
$LaPO_4$ [cr]	233.8769 {a}	45.679 {k}		**-1955.2 (2.1) {b}**		**-306 (2)**	
$CePO_4$ [cr]	235.0914 {a}	44.695 {k}		**-1959.5 (4.6) {b}**		**-309 (2)**	
$NdPO_4$ [cr]	239.2114 {a}	43.554 {k}		**-1960.4 (2.0) {b}**		**-304 (2)**	
$EuPO_4$ [cr]	246.9314 {a}	42.02 {k}		**-1850.1 (5.1) {b}**		**-272 (3)**	
$YbPO_4$ [cr]	268.0114 {a}	41.73 {k}		**-1966.1 (2.3) {b}**		**-261 (2)**	
$LuPO_4$ [cr]	269.9384 {a}	41.33 {k}		**-1582.6 (2.5)**		**-256 (2.5)**	
$PuPO_4$ [cr]	334.0236 {a}			***-1916 (14) {b}***		***-264 (14) {be}***	
UPO_4 [cr]	333.0003 {a}			***-1752 (17) {b}***		***-272.7 (14) {be}***	
$AmPO_4$ [cr]	337.9714 {a}			***-1888 (15) {b}***		***-273 (14) {be}***	
Other Phases							
$CaTiO_3$ [cr, perovskite]	134.9582 {a}	33.69 {b}	**93.3 (0.2)**	**-1660.8 (3.3)**	**-1575.3 (3.3)**	**-81.7 (2.9)**	

Compound name [phase, allotrope]	Mw $g \cdot mol^{-1}$	V^o $cm^3 \cdot mol^{-1}$	S^o $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H^o$ $kJ \cdot mol^{-1}$	$\Delta_f G^o$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(1)$ $kJ \cdot mol^{-1}$	$\Delta_r H^o(2)$ $kJ \cdot mol^{-1}$
$ZrTiO_4$ [cr]	202.0976 {a}	39.95 {b}	**111.0 (0.2)**	**-2023.8 (4.2)**	**-1913.8 (4.3)**	**+20.5 (4.1) {d}**	
$HfTiO_4$ [cr]	289.3676 {a}	40.07 {b}		{c}		{c}	

Notes to table 3.

a. Value calculated by the authors from data found in a publication referenced by Putnam et al. (Putnam 2001).
b. Value calculated by the authors for this work.
c. Measured data forthcoming in a future publication.
d. Metastability predicted or potential for metastability is predicted based on the value and its error margins.
e. Estimated using systematic trends described by Putnam in (Ph.D. Putnam 1999).
f. Values of S are estimated based on assumed sample stability at a synthesis temperature of 1623 K (synthesis temp of Ce, U, and Th brannerite samples). Values of G are calculated based on entropy stabilization from binary oxides at 1623 K.
g. Published results corrected for improper conversion from calories to J. as noted by the authors through personal communication.
h. Uses a linear free energy relationship to predict the Gibbs free energy of formation as noted by Xu (Xu1999).
i. Predicted definitely to be metastable with respect to decomposition. Delta G for CeO2 + SiO2 = CeSiO4 is calculated to be +7.1 (2.1) at 298.15 K.
j. Predicted to possibly be metastable with respect to decomposition. Delta G for PuO2 + SiO2 = PuSiO4 is calculated to be -0.11 (1.2) at 298.15 K.
k. Calculated for this work from data found in another reference found in this work.

4.2 Publications

Table 4. Publications resulting from this study.

1. "Thermodynamics of Formation for Zirconolite, $CaZrTi_2O_7$, From T = 298 K to T = 1500 K." *J. Chem. Thermodynamics* **1999**, 31, 3, 229-243. R. L. Putnam, A. Navrotsky, B. F. Woodfield, J. Boerio-Goates, J. L. Shapiro.
2. "Molar Heat Capacity and Thermodynamic Functions of Zirconolite, $CaZrTi_2O_7$." *J. Chem. Thermodynamics* **1999**, 31, 3, 245-253. B. F. Woodfield, J. Boerio-Goates, J. L. Shapiro. R. L. Putnam, A. Navrotsky.
3. "Heat capacity, third law entropy, and formation energetics of zirconolite, $CaZrTi_2O_{7.}$" R. L. Putnam, A. Navrotsky, B. F. Woodfield, J. L. Shapiro, and J. Boerio-Goates *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries IV*; eds. J. C. Marra and G. T. Chandler; The American Ceramic Society; Westerville, OH **1999**, 93, 339-347.
4. "Thermochemistry of Hf-zirconolite, $CaHfTi_2O_7$." R. L. Putnam, A. Navrotsky, B. F. Woodfield, J. L. Shapiro, R. Stevens, and J. Boerio-Goates *Mat. Res. Soc. Proc.* **1999**, 556,11-18.
5. "Molar Heat Capacity and Thermodynamic Functions for $CaTiO_3$." *J. Chem. Thermodynamics* **1999**, 31, 12, 1573-1583. B. F. Woodfield, J. L. Shapiro, R. Stevens, J. Boerio-Goates. R. L. Putnam, K. B. Helean, A. Navrotsky.
6. "Thermodynamics of formation for two cerium aluminum oxides, $CeAlO_3$ and $CeAl_{12}O_{19.918}$, and cerium sesquioxide, Ce_2O_3 at T = 298.15 K." *J. Chem. Thermodynamics* **2000**, 32, 7, In Press. R. L. Putnam, A. Navrotsky, E. H. P. Cordfunke, M. E. Huntelaar.
7. "Microstructure and Composition of Synroc Samples Crystallized from a $CaCeTi_2O_7$ Chemical System: HRTEM/EELS Investigation." *Mat. Res. Soc. Proc.* **In Press - 2000** H. Xu, Y. Wang, R. L. Putnam, J. Gutierriez, A. Navrotsky.

8. "The Thermodynamics of Formations, Molar Heat Capacity, and Thermodynamic Functions of $ZrTiO_4$ (cr)." *J. Chem. Thermodynamics* **In Press 2001**. B. K. Hom, R. Stevens, B. F. Woodfield, J. Boerio-Goates, R. L. Putnam, K. B. Helean, A. Navrotsky.
9. "Thermodynamics of Formation for Hf-Zirconolite, $CaHfTi_2O_7$(cr) and HfO_2(cr) from T = 0 K to T = 1500 K; Revised values of $\Delta_f^T G_m^o$ for $CaZrTi_2O_7$(cr) over the same temperature." *J. Chem. Thermodynamics* **Submitted 12/00**. R. L. Putnam, J. Gutierriez, A. Navrotsky, R. Stevens, B. K. Hom, J. Boerio-Goates., and B. F. Woodfield.
10. "The Molar Heat Capacity and Thermodynamic Functions of $CaHfTi_2O_7$(cr) and the Solid Solution $CaZr_{0.26}Hf_{0.74}Ti_2O_7$(cr); New Values for the Entropy of $CaZrTi_2O_7$(cr)." *J. Chem. Thermodynamics* **Submitted 12/00** R. Stevens, B. K. Hom, J. Boerio-Goates., B. F. Woodfield, R. L. Putnam, J. Gutierriez, and A. Navrotsky.
11. "Formation energetics of ceramic phases related to surplus plutonium disposition." R. L. Putnam, B. B. Ebbinghaus, A. Navrotsky, K. B. Helean, S. V. Ushakov, B. F. Woodfield, J. Boerio-Goates *Ceramic Transactions* Proceedings of the 102nd American ceramic Society, symposium B5. St. Louis, MO April 2000. Volume edited by D. Spearing and R.L. Putnam. **In press for early 2001**.
12. "Systematic Trends and Prediction of Enthalpies of Formation of Refractory Lanthanide and Actinide Ternary Oxide Phases." A. Navrotsky. *Ceramic Transactions* Proceedings of the 102nd American ceramic Society, symposium B5. St. Louis, MO April 2000. Volume edited by D. Spearing and R.L. Putnam. **In press for early 2001**.
13. "Enthalpies of Formation of Gd2(Ti2-xZrx)O7 Pyrochlores", K. B. Helean, B. D. Begg, A. Navrotsky, B. Ebbinghaus, W. J. Webber, and R. C. Ewing, Mat. Res. Soc. Proc. (**submitted 12/ 2000**).
14. Ph.D. Dissertation: Princeton University **November 1999**, R. L. Putnam.

4.3 Participation

Table 5. Individuals supported by / or contributing to this project.

Individual	Designation	Location
Mark A. Williamson	Principle Investigator - Technical Staff Member	Los Alamos National Laboratory
John Huang	Co-Principle Investigator- Technical Staff Member	Los Alamos National Laboratory
Dane Spearing	Post Doctoral Staff Member	Los Alamos National Laboratory
Robert L. Putnam	Post Doctoral Staff Member – Technical Staff Member	Los Alamos National Laboratory
Ubaldo Gallegos	Technical Staff Member	Los Alamos National Laboratory
Alexandra Navrotsky	Co-Principle Investigator – Professor	University of California, Davis
Sergey Ushakov	Post Doctoral Researcher	University of California, Davis
Matia Howlader	Post Doctoral Researcher	University of California, Davis
Robert L. Putnam	Graduate Student	University of California, Davis
Katheryn B. Helean	Graduate Student	University of California, Davis
Vladimir Kodash	Graduate Student	University of California, Davis
Theresa Lee	Graduate Student	University of California, Davis
April Martinez	Graduate Student	University of California, Davis
Jose Gutierriez	High School Student	University of California, Davis
Bartley B. Ebbinghaus	Co-Principle Investigator	Lawrence Livermore National Laboratory
James M Lawson	Sample characterization	Lawrence Livermore National Laboratory
Robert P. Gomez	Sample Fabrication	Lawrence Livermore National Laboratory
Thomas E. Macari	Sample Fabrication	Lawrence Livermore National Laboratory
Walter L. Close III	Sample Fabrication	Lawrence Livermore National Laboratory

5.0 Summary of recent progress and future direction at individual institutions

5.1 Los Alamos National Laboratory, LANL

The installation and initial prove-in process for the LANL high-temperature solution calorimeter has been completed by Putnam and the instrument is ready for the study of actinide-bearing materials. Funding is being sought to examine the Pu-pyrochlore which has recently been synthesized and characterized at LLNL by Ebbinghaus. Further studies in actinide-bearing oxide materials and pyrochlore structured materials have been started with collaboration with Sickafus (Sickafus 2000). Additionally the calorimeter will be used in phase studies of actinide metal alloys.

5.2 University of California at Davis, UCD

K.B. Helean's Ph.D. thesis is progressing well, and it is expected to be completed about a year from now. In order to provide reliable data on rare-earth containing phases (pyrochlores, fluorite-based materials, phosphates, silicates) the enthalpies of solution of the rare earth oxides in our calorimetric solvents must be well known. Because of hygroscopicity, polymorphism, and somewhat slow solution kinetics, these values need to be crosschecked using several solvents and methods to assure accuracy and precision. This work is now complete and forms the basis of a number of papers to be written in the next few months. Similarly, calorimetric data for UO_2 and ThO_2 are now secure, and work on brannerites containing these elements is essentially complete. The experience gained in using the lanthanide and U and Th oxides is crucial before the Los Alamos calorimetry effort goes on to tackle oxides of Pu and other actinides. Work on cerium pyrochlore is complete and that on a nonstoichiometric U-pyrochlore is finished except for some additional electron microprobe analysis. A series of $Gd_2Zr_2O_7$-$Gd_2Ti_2O_7$ pyrochlores have been made, as well as a mainly disordered gadolinium titanate. Calorimetry on these samples is in the final stages and the energetics are being analyzed in terms of heats of mixing and order-disorder phenomena. The disordered pyrochlores are in fact cubic zirconia (fluorite structure) phases similar to those encountered as solid electrolytes. Theresa Lee, a postdoc, is working on their energetics. Because of the possible relation between ease of disordering and radiation resistance, as stressed by Sickafus at Los Alamos and Ewing at Michigan, understanding the energetics of both ordered pyrochlores and disordered fluorites is very important. A set of rare earth titanate pyrochlores, provided by Lynn Boatner at Oak Ridge, will explore this relation further, as well as studies on $Gd_2Hf_2O_7$ in collaboration with Putnam and Sickafus at Los Alamos. Postdoc Sergey Ushakov is involved in this work.

Rare earth phosphates, $REPO_4$, are potential actinide hosts and are important secondary phases in the corrosion of actinide bearing glasses and ceramics in the

natural environment. Ushakov has completed a systematic study of their energetics using a set of single crystal samples provided by Boatner.

This next year will be one of completing calorimetry on pyrochlores and writing papers. What remains to be done at Davis is a systematic study relating order disorder, energetics, and radiation damage studies done elsewhere. This area, linking pyrochlore and fluorite studies, has impact both for the radiation resistance and durability of waste forms and for the use of the very similar disordered phases as solid electrolytes in oxide fuel cells and oxygen separation membranes. In both cases, fundamental thermochemical data are essential to assessing materials compatibility, degradation in use, and optimum synthesis routes. The thermodynamic data are necessary input into kinetic models of dissolution and decomposition. Without such fundamental data, commercial processes rest on uncertain ground as to the final states of the materials they produce and utilize.

5.3 Lawrence Livermore National Laboratory ,LLNL

At LLNL the focus of the work was to fabricate two Pu-bearing minerals and send them to LANL for drop solution calorimetry. Under funding provided by the PIP, a number of other non-Pu bearing phases were also prepared and sent to UCD for drop solution calorimety. The two Pu-bearing samples selected for this work are a Pu brannerite, nominally $PuTi_2O_6$, and a Pu-pyrochlore, nominally $CaPuTi_2O_7$. Ultimately the preparation of the Pu brannerite was unsuccessful. The sample was lost after the sixth heat treatment when one of the crucibles of containment melted in the furnace. The preparation of the Pu pyrochlore was marginally successful. A sample containing greater than 90 vol % pyrochlore was obtained. The balance of the material was a quantifiable amount of essentially pure PuO_2 and TiO_2. Although suitable for drop solution calorimetry, the sample was not fabricated in time to conduct the drop solution measurements as part of this work.

6.0 References

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7.0 Appendix

