Thermodynamic assessment of the oxygen rich U-Ce-O system

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ABSTRACT

A thermodynamic assessment of the U-Ce-O system was performed by combining the existing Calphad assessments of the U-O and Ce-O binaries. A compound energy formalism representation for the fluorite $U_{1-y}Ce_yO_{2\pm x}$ and a partially ionic two-sublattice liquid model for U-Ce-O melt were developed to describe the ternary solutions. Oxygen potentials for $U_{1-y}Ce_yO_{2\pm x}$ for 0.05, 0.20, 0.30, and 0.50 Ce metal fractions were measured from thermogravimetric analysis and used, along with other thermodynamic data reported in the literature, to optimize the adjustable parameters of the models for $U_{1-y}Ce_yO_{2\pm x}$ and the U-Ce-O ternary liquid. In addition, the thermochemical behavior of $U_{1-y}Ce_yO_{2\pm x}$ and $U_{1-y}Pu_yO_{2\pm x}$ was compared in order to assess the suitability of using Ce as a surrogate for Pu in MOX fuel.

Keywords: $UO_{2\pm x}$, uranium, cerium, oxygen, compound energy formalism, Calphad, oxygen potential, phase equilibria

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1. Introduction

Thermodynamic models of the phases in the U-Ce-O system are essential for understanding the chemistry and predicting the behavior of UO_2 based nuclear fuel. Cerium is a high yield fission product (FP) that dissolves extensively in the UO_2 matrix in turn affecting many of its properties. The U-Ce-O system is also of interest since Ce may be used as a surrogate for Pu for studying mixed oxide (MOX) fuel. Since CeO_2 and PuO_2 are isostructural, the 3+ and 4+ oxidation states predominate for both Ce and Pu, and the two have comparable ionic radii [1]. The rationale is Ce and Pu dissolved in urania, i.e. $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ and $\text{U}_{1-y}\text{Pu}_y\text{O}_{2\pm x}$ solutions, behave in a chemically similar way. It is therefore important to compare the phase equilibria and thermochemistry of $\text{U}_{1-y}\text{Pu}_y\text{O}_{2\pm x}$ and $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$. Since UO_2 is the dominant phase in conventional reactor fuel and Ce is a high yield FP, understanding the phase with dissolved Ce is essential for predicting its behavior. Thus, the aim of the effort reported here is a CALPHAD (Calculation of Phase Diagrams) [2, 3] assessment of the U-Ce-O to aid in establishing the suitability of Ce as a surrogate for Pu in MOX studies. Further, since phase field and continuum scale transport modeling uses thermodynamics for key inputs, this work also supports physics-based fuel performance simulations.

2. Literature review

In the Calphad approach, the chemical and physical properties of the phases in a system are considered along with all of the available data when choosing models and optimizing their adjustable parameters. This facilitates representations that can be extrapolated outside of their range of experimental validation with a higher degree of confidence [3]. Therefore, a critical evaluation of the available data to be used for model refinement is a crucial part of a thermodynamic assessment.

A literature review revealed studies reporting oxygen potentials (μ_{O_2}) for $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ [4-13], which are summarized in Table 1, along with molar heat capacity (C_p) measurements for stoichiometric $\text{U}_{1-y}\text{Ce}_y\text{O}_{2.00}$ [1, 14, 15]. Lorenzelli and Touzelin [8], Markin et al. [16], and Hoch and Furman [6] used X-ray diffraction (XRD) to determine the phase relations in the vicinity of the fluorite $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ solution. Nawada et al. [17] conducted XRD measurements of $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ in air from 873 – 1273 K over the 2.5 to 90 atomic % Ce compositional range. The proposed phase diagrams resulting from these studies are shown in Fig. 1. Finally, some limited ternary melting measurements have been determined by Valdez and Byler [18] and Adamson et al. [19].

A sufficient number of works reporting oxygen potentials for $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ made comparisons between authors possible. The data from Lorenzelli and Touzelin [8], Norris and Kay [11], Markin and Crouch [9], Ducroux and Baptiste [5], and Kang et al. [7] were judged to be a consistent. However, the measurements made by Hoch and Furman [6] were higher while those of Nagarajan et al. [10] were lower compared to the majority of values from other studies determined under equivalent or similar conditions. Much of the data determined by Brown [4] were internally inconsistent due to experimental repeatability issues.

3. Experimental

The vast majority of μ_{O_2} measurements considered reliable were made at Ce compositions corresponding to $y \geq 0.30$. To supplement this existing body of work and to aid in determining a reliable subset of that data, thermogravimetric analysis (TGA) of equilibrium p_{O_2} as a function of Ce content, oxygen-to-metal

ratio (O/M), and temperature were conducted for $y = 0.0, 0.05, 0.20, 0.30,$ and 0.50 at Oak Ridge National Laboratory (ORNL) and Los Alamos National Laboratory (LANL).

3.1 Sample preparation by the Modified Direct Denitration method

A Modified Direct Denitration (MDD) [20] method was used to prepare the $U_{1-y}Ce_yO_{2\pm x}$ samples for TGA at ORNL. Known ratios of UO_2 and CeO_2 starting materials were dissolved in nitric acid (HNO_3) and heated to ~ 353 K to form the metal nitrate $U_{1-y}Ce_yO_{2\pm x}(NO_3)_2$. Ammonium nitrate was then added to produce a double salt given by $(NH_4)_2 U_{1-y}Ce_yO_{2\pm x}(NO_3)_4$ which was subsequently denitrated in a rotary kiln at ~ 600 K to yield a free flowing intimately mixed powder of fully oxidized metals, i.e. UO_3 and CeO_2 . The powder was then pressed and thermally treated in an appropriate oxygen atmosphere to both sinter and adjust the oxygen stoichiometry in order to form 500-1500 mg $U_{1-y}Ce_yO_{2.000}$ solid solution; the method for determining the p_{O_2} required to achieve an $O/M = 2.000$ is discussed in detail in the next section. Sample purity for this method has been benchmarked with inductively coupled plasma mass spectrometry (ICP-MS) analysis which shows negligibly small quantities of foreign matter are introduced during the process.

For this work, 775 mg – 2300 mg samples corresponding to $U_{0.95}Ce_{0.05}O_{2\pm x}$, $U_{0.80}Ce_{0.20}O_{2\pm x}$, $U_{0.70}Ce_{0.30}O_{2\pm x}$, and $U_{0.50}Ce_{0.50}O_{2\pm x}$ were prepared by the MDD method discussed above. Upon conditioning to an $O/M = 2.000$, XRD analysis was performed to confirm both the composition and the existence of a single phase FCC solid solution.

3.2 Sample preparation by solid state reaction

Samples analyzed by TGA at LANL were prepared using conventional power processing techniques. First, feedstocks of stoichiometric UO_2 and CeO_2 were blended in the required ratios. Uranium dioxide powder was reduced under an Ar-6% H_2 environment (~ 1200 K for 4 hours) to obtain an O/M of 2.000. Cerium dioxide powder was calcined in ambient air (~ 1100 K for 4 hours) to ensure that the material was fully oxidized. Stoichiometry of both feedstocks was verified through both XRD and TGA.

The requisite ratios of UO_2 and CeO_2 were combined and co-milled with a high-energy ball mill using an alumina jar and alumina media for 15 minutes to adequately intermix the powders. Total batch sizes were approximately 20 grams. The resulting UO_2 - CeO_2 feedstock was then sieved using a -325 mesh and pressed into green compacts using a manual hydraulic press. The pressing pressure used was approximately 300 MPa, and pressure was held for approximately 60 seconds. The pellet sizes used in this study were approximately 5.6 mm in diameter, 3.5 mm in height, and weighed between 750 and 850 mg.

Homogenization was achieved through use of a two-step sintering and subsequent stoichiometric adjustment. Sintering was performed in either CO_2 or Ar-6% H_2 atmospheres. These variations were included to assess the impact of oxidizing versus reducing atmospheres on the sintering kinetics of the U-Ce-O system, but discussion of observations with respect to this variable are deferred to a later publication.

Densification under a CO_2 atmosphere was achieved following a hold of 8 h at 1773 K in an alumina tube furnace, while sintering under a reducing environment utilized holds of 20 h at 2028 K in an exposed

element tungsten furnace. Cooling to room temperature from the 2028 K isotherm under the reducing atmosphere was performed under pure argon to avoid potential reduction of the cerium. The high oxygen potential of CO₂ at the sintering temperature and low potential of the Ar-6% H₂ atmosphere resulted in significant hyperstoichiometry and hypostoichiometry, respectively in the as-sintered pellets. An O/M adjustment was therefore performed to obtain an O/M of 2.000 in the TGA prior to execution of any oxygen potential measurements. An oxygen potential of -368 kJ/mol at 1123 K was found capable of this adjustment to O/M = 2.000 following a 24 hour hold for both the U_{0.80}Ce_{0.20}O₂ and U_{0.70}Ce_{0.30}O₂ compositions. Both sintering methods yielded specimens of acceptable density (90-95% TD) measured geometrically following stoichiometric adjustment. Full homogenization to a single FCC phase was confirmed by XRD performed on powder samples obtained by pulverizing the sintered and adjusted material. This result validated the use of samples produced by both methods for the purposes of the current work.

3.3 Thermogravimetric technique

Nearly identical Netzsch STA 449 F1 Jupiter[®] scanning thermal analyzers were used to measure the relationship between the equilibrium oxygen partial pressures (p_{O_2}), temperature, and O/M for the U_{1-y}Ce_yO_{2+x} solid solutions at both ORNL and LANL. For a sample of known U/Ce ratio, the temperature was controlled by the STA 449 F1 while the p_{O_2} was fixed at ORNL by an Environics[®] Series 2000 Computerized Multi-Component Gas Mixer by combining H₂ and O₂ or H₂ and H₂O gases in appropriate ratios. Oxygen partial pressure was controlled at LANL using a slightly different approach. Tanks containing calibrated H₂ contents (nominally 100 and 1000 parts per million H₂) were flowed over a water bath maintained at controlled temperatures in the 275-290 K range. Differences in the evolved H₂/H₂O ratio obtained by control the H₂ content in the gas stream and the temperature of the water bath provided a means to control the p_{O_2} in the range necessary for this study. The calculated p_{O_2} was verified by measuring the effluent gas stream from the STA 449 F1 with either a Centorr[®] Oxygen Monitor Model 2D (ORNL) or a Cambridge Sensotec Rapidox 3100 OEM Oxygen Analyzer (LANL).

The sample was placed in an alumina crucible from Netzsch instruments in a furnace lined with an alumina protective tube and heated with a silicon carbide or high temperature graphite resistance element. The mass change was electronically measured by a microbalance with a sensitivity of ±0.025 μg and equilibrium was judged to occur when the rate of mass change was within the reported drift tolerance of the instrument (±10 μg/hr). The measurements were analyzed using the STA 449 F1 Proteus[®] data acquisition software.

The TGA technique for determining the equilibrium p_{O_2} relationship with composition and temperature for nonstoichiometric oxides is well documented in the literature, see for example [21, 22]. In brief, the mixed oxide sample was initially conditioned to a reference (O/M^{REF}), usually an O/M = 2.000. The mass change (Δm) from the reference to equilibrium with a designated oxygen pressure was used to calculate the resulting O/M change from the relation given by Eqn. 1 where mw_s and $mass_s$ are the molecular weight and mass of the mixed oxide respectively at the stoichiometry corresponding to O/M^{REF} .

$$O / M = O / M^{REF} + \frac{mw_s \times (\Delta m)}{16 \frac{g}{mol} \times mass_s} \quad 1$$

The experimental procedure was first validated using a ~500 mg sample of urania free of impurities and compared to measurements of Lindemer and Sutton [21] and Aronson and Belle [23]. Figure 2 shows that the agreement is very good and that the thermogravimetric method used in this work yields results consistent with accepted studies.

The uncertainty in the log p_{O_2} settings were determined by estimating the propagation of independent random errors [24] from gas compositions, flow settings, and the thermocouple readings. The repeatability of the microbalance was $\pm 40 \mu\text{g}$ yielding an O/M to an accuracy of ± 0.0007 for a 1000 mg sample.

4. Modeling

This work uses the models for the phases in the binary U-O and Ce-O systems from the work of Guéneau et al. [25] and Zinkevich et al. [26] respectively. In the Ce-O assessment, the Ce metal allotropes, the sesquioxide $\text{Ce}_2\text{O}_{3-x}$ polymorphs, bixbyite $\text{Ce}_3\text{O}_{5\pm x}$, and fluorite CeO_{2-x} are described with an oxygen homogeneity range. For this work, the only ternary phases are considered to be $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$, $(\text{U,Ce})_3\text{O}_8$ and the U-Ce-O melt. In the current effort, pressure independent Gibbs energy is assumed, except for the vapor, and all species are referred to the enthalpy and entropy of formation from their stable elements at standard state conditions of 298.15 K and 1 atm. FactSage computational thermodynamic software [27] was used for equilibrium calculations and parameter optimizations.

4.1 The vapor phase

The vapor phase in the U-Ce-O system is considered to consist of O, O_2 , O_3 , U, UO, UO_2 , UO_3 , Ce, Ce_2 , CeO, and CeO_2 . The reference molar Gibbs energy functions for Ce, Ce_2 , CeO, U, O, O_3 and O_2 are taken from the SGTE Substances Database Version 2 [28] while those for UO, UO_2 , UO_3 , and CeO_2 are taken from the work of Konings et al. [29].

4.2 Pure elements and stoichiometric phases

The compounds U_4O_9 and UO_3 are treated as stoichiometric phases after Guéneau et al. [25, 30] as well as Ce_7O_{12} , Ce_9O_{16} , $\text{Ce}_{11}\text{O}_{20}$, $\text{Ce}_{19}\text{O}_{34}$, $\text{Ce}_{40}\text{O}_{72}$, and $\text{Ce}_{62}\text{O}_{112}$ which come from the assessment by Zinkevich [31]. Elemental U values are from the SGTE database [28].

4.3 The liquid phase

The partially ionic two-sublattice model (TSLM) [32] for U-O from Guéneau et al. [25] is combined with the TSLM for Ce-O from Zinkevich et al. [26]. The sublattice representation is:

In order to maintain charge neutrality over the entire ternary compositional space, the TSLM defines P and Q using the following equations:

$$P = \sum_A \nu_A y_A + Q y_{\text{Va}} \quad 2$$

$$Q = \sum_C \nu_C y_C \quad 3$$

where ν_A and y_A are the charge and site fraction of the anion species and ν_C and y_C are the charge and site fraction of the cation C , respectively; and y_{Va} is the site fraction for a vacancy of charge Q .

The molar Gibbs energy of the liquid phase is thus:

$$\begin{aligned} G^{\text{liq}} = & y_{\text{Ce}^{3+}} y_{\text{O}^{2-}} {}^\circ G_{\text{Ce}_2\text{O}_3}^{\text{liq}} + y_{\text{Ce}^{4+}} y_{\text{O}^{2-}} 2 {}^\circ G_{\text{CeO}_2}^{\text{liq}} + y_{\text{U}^{4+}} y_{\text{O}^{2-}} 2 {}^\circ G_{\text{UO}_2}^{\text{liq}} \\ & + Q \left[y_{\text{Va}^{\text{Q-}}} \left(y_{\text{Ce}^{3+}} {}^\circ G_{\text{Ce}^{3+};\text{Va}^{\text{Q-}}}^{\text{liq}} + y_{\text{Ce}^{4+}} {}^\circ G_{\text{Ce}^{4+};\text{Va}^{\text{Q-}}}^{\text{liq}} + y_{\text{U}^{4+}} {}^\circ G_{\text{U}^{4+};\text{Va}^{\text{Q-}}}^{\text{liq}} \right) + y_{\text{O}} {}^\circ G_{\text{O}}^{\text{liq}} \right] \\ & + RTP \left(y_{\text{Ce}^{3+}} \ln y_{\text{Ce}^{3+}} + y_{\text{Ce}^{4+}} \ln y_{\text{Ce}^{4+}} + y_{\text{U}^{4+}} \ln y_{\text{U}^{4+}} \right) \\ & + RTQ \left(y_{\text{O}^{2-}} \ln y_{\text{O}^{2-}} + y_{\text{Va}^{\text{Q-}}} \ln y_{\text{Va}^{\text{Q-}}} + y_{\text{O}} \ln y_{\text{O}} \right) \\ & + {}^{\text{xs}} G^{\text{liq}} \end{aligned} \quad 4$$

where T is the absolute temperature and R is the ideal gas constant. The Gibbs functions, ${}^\circ G_i^{\text{liq}}$, for the Ce containing end-members come from [26] while the neutral O and those with U cations are taken from [25].

The molar excess Gibbs energy term, ${}^{\text{xs}} G^{\text{liq}}$, is described with the zeroth, first and second order interaction parameters from a Redlich-Kister [33] polynomial expansion:

$$\begin{aligned} {}^{\text{xs}} G^{\text{liq}} = & y_{\text{Ce}^{3+}}^i y_{\text{Ce}^{4+}}^i y_{\text{O}^{2-}}^{ii} \left[{}^0 L_{\text{Ce}^{3+};\text{Ce}^{4+};\text{O}^{2-}}^{\text{liq}} + \left(y_{\text{Ce}^{3+}}^i - y_{\text{Ce}^{4+}}^i \right) \left({}^1 L_{\text{Ce}^{3+};\text{Ce}^{4+};\text{O}^{2-}}^{\text{liq}} \right) \right] \\ & + y_{\text{Ce}^{3+}}^i y_{\text{O}^{2-}}^i y_{\text{Va}}^{ii} {}^0 L_{\text{Ce}^{3+};\text{O}^{2-};\text{Va}}^{\text{liq}} \\ & + y_{\text{U}^{4+}}^i y_{\text{O}^{2-}}^{ii} y_{\text{Va}}^{ii} \left[{}^0 L_{\text{U}^{4+};\text{O}^{2-};\text{Va}}^{\text{liq}} + \left(y_{\text{O}^{2-}}^{ii} - y_{\text{Va}}^{ii} \right) \left({}^1 L_{\text{U}^{4+};\text{O}^{2-};\text{Va}}^{\text{liq}} \right) + \left(y_{\text{O}^{2-}}^{ii} - y_{\text{Va}}^{ii} \right)^2 \left({}^2 L_{\text{U}^{4+};\text{O}^{2-};\text{Va}}^{\text{liq}} \right) \right] \\ & + y_{\text{Ce}^{3+}}^i y_{\text{U}^{4+}}^i y_{\text{O}^{2-}}^{ii} {}^0 L_{\text{Ce}^{3+};\text{U}^{4+};\text{O}^{2-}}^{\text{liq}} + y_{\text{Ce}^{4+}}^i y_{\text{U}^{4+}}^i y_{\text{O}^{2-}}^{ii} {}^0 L_{\text{Ce}^{4+};\text{U}^{4+};\text{O}^{2-}}^{\text{liq}} \end{aligned} \quad 5$$

The adjustable parameters are the interaction terms ${}^0L_{Ce^{3+},U^{4+},O^{2-}}^{liq}$ and ${}^0L_{Ce^{3+},O^{2-},Va}^{liq}$ with the remainder of the terms adopted from the assessments of U-O [25] and Ce-O[26].

4.4 The fluorite $U_{1-y}Ce_yO_{2\pm x}$ phase

Guéneau et al. [25] used a three sublattice CEF to represent non-stoichiometric urania while Zinkevich et al. [26] used a two sublattice CEF for ceria. In order to combine the two for a unified $U_{1-y}Ce_yO_{2\pm x}$ description, a three sublattice CEF for CeO_{2-x} was developed that yielded equivalent phase equilibria, oxygen potential, and heat capacity as the model from [26] as can be seen in Figs. 3-4. Thus, the CEF for $U_{1-y}Ce_yO_{2\pm x}$ is represented with three sublattices as follows:

The CEF Gibbs energy for the $U_{1-y}Ce_yO_{2\pm x}$ solid solution can be written as:

$$\begin{aligned} G^F = & y_{U^{3+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{3+},O:O}^F + y_{U^{3+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{3+},O:Va}^F + y_{U^{3+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{3+},Va:O}^F + y_{U^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{3+},Va:Va}^F \\ & + y_{U^{4+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{4+},O:O}^F + y_{U^{4+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{4+},O:Va}^F + y_{U^{4+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{4+},Va:O}^F + y_{U^{4+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{4+},Va:Va}^F \\ & + y_{U^{5+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{5+},O:O}^F + y_{U^{5+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{5+},O:Va}^F + y_{U^{5+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{5+},Va:O}^F + y_{U^{5+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{5+},Va:Va}^F \\ & + y_{U^{6+}}^i y_O^{ii} y_O^{iii} \circ G_{U^{6+},O:O}^F + y_{U^{6+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{U^{6+},O:Va}^F + y_{U^{6+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{U^{6+},Va:O}^F + y_{U^{6+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{U^{6+},Va:Va}^F \\ & + y_{Ce^{3+}}^i y_O^{ii} y_O^{iii} \circ G_{Ce^{3+},O:O}^F + y_{Ce^{3+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{Ce^{3+},O:Va}^F + y_{Ce^{3+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{Ce^{3+},Va:O}^F + y_{Ce^{3+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{Ce^{3+},Va:Va}^F \\ & + y_{Ce^{4+}}^i y_O^{ii} y_O^{iii} \circ G_{Ce^{4+},O:O}^F + y_{Ce^{4+}}^i y_O^{ii} y_{Va}^{iii} \circ G_{Ce^{4+},O:Va}^F + y_{Ce^{4+}}^i y_{Va}^{ii} y_O^{iii} \circ G_{Ce^{4+},Va:O}^F + y_{Ce^{4+}}^i y_{Va}^{ii} y_{Va}^{iii} \circ G_{Ce^{4+},Va:Va}^F \\ & + RT \left[\left(y_{U^{3+}}^i \ln y_{U^{3+}}^i + y_{U^{4+}}^i \ln y_{U^{4+}}^i + y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i + y_{Ce^{3+}}^i \ln y_{Ce^{3+}}^i + y_{Ce^{4+}}^i \ln y_{Ce^{4+}}^i \right) \right. \\ & \left. + 2 \left(y_O^{ii} \ln y_O^{ii} + y_{Va}^{ii} \ln y_{Va}^{ii} \right) + \left(y_O^{iii} \ln y_O^{iii} + y_{Va}^{iii} \ln y_{Va}^{iii} \right) \right] \\ & + {}^{xs}G^F \end{aligned} \tag{6}$$

The model for the $U_{1-y}Ce_yO_{2\pm x}$ phase from this work uses the thermodynamic functions for the $UO_{2\pm x}$ CEF representation developed by Guéneau et al. [25] and those for the U^{6+} containing end-member additions from [34]. The excess molar Gibbs energy, expressed as an expansion of the Redlich-Kister [33] polynomial in terms of site fractions, is represented as:

$$\begin{aligned}
{}^{xs}G^F = & y_{Va}^{ii} y_{Va}^{iii} \left(\begin{aligned} & y_{U^{4+}}^i y_{Ce^{3+}}^i {}^0L_{U^{4+},Ce^{3+},Va:Va}^F + y_{U^{4+}}^i y_{Ce^{3+}}^i (y_{U^{4+}}^i - y_{Ce^{3+}}^i) {}^1L_{U^{4+},Ce^{3+},Va:Va}^F \\ & + y_{U^{4+}}^i y_{Ce^{4+}}^i {}^0L_{U^{4+},Ce^{4+},Va:Va}^F + y_{U^{4+}}^i y_{Ce^{4+}}^i (y_{U^{4+}}^i - y_{Ce^{4+}}^i) {}^1L_{U^{4+},Ce^{4+},Va:Va}^F \\ & + y_{U^{5+}}^i y_{Ce^{4+}}^i {}^0L_{U^{5+},Ce^{4+},Va:Va}^F + y_{U^{4+}}^i y_{Ce^{4+}}^i (y_{U^{4+}}^i - y_{Ce^{4+}}^i) {}^1L_{U^{4+},Ce^{4+},Va:Va}^F \\ & + y_{Ce^{3+}}^i y_{Ce^{4+}}^i {}^0L_{Ce^{3+},Ce^{4+},Va:Va}^F + y_{Ce^{3+}}^i y_{Ce^{4+}}^i (y_{Ce^{3+}}^i - y_{Ce^{4+}}^i) {}^1L_{Ce^{3+},Ce^{4+},Va:Va}^F \end{aligned} \right) \\
& + y_{Va}^{ii} y_{Va}^{iii} \left(\begin{aligned} & y_{U^{3+}}^i y_{U^{4+}}^i {}^0L_{U^{3+},U^{4+},O:Va}^F + y_{U^{3+}}^i y_{U^{4+}}^i (y_{U^{3+}}^i - y_{U^{4+}}^i) {}^1L_{U^{3+},U^{4+},O:Va}^F \\ & + y_{U^{3+}}^i y_{Ce^{3+}}^i {}^0L_{U^{3+},Ce^{3+},O:Va}^F + y_{U^{4+}}^i y_{Ce^{4+}}^i {}^0L_{U^{4+},Ce^{4+},O:Va}^F + y_{U^{5+}}^i y_{Ce^{4+}}^i {}^0L_{U^{5+},Ce^{4+},O:Va}^F \\ & + y_{Ce^{3+}}^i y_{Ce^{4+}}^i {}^0L_{Ce^{3+},Ce^{4+},O:Va}^F + y_{Ce^{3+}}^i y_{Ce^{4+}}^i (y_{Ce^{3+}}^i - y_{Ce^{4+}}^i) {}^1L_{Ce^{3+},Ce^{4+},O:Va}^F \end{aligned} \right) \\
& + y_{U^{4+}}^i y_{U^{5+}}^i y_{O}^{ii} y_{O}^{iii} {}^0L_{U^{4+},U^{5+},O:O}^F + y_{O}^{ii} y_{O}^{iii} (y_{U^{5+}}^i y_{Ce^{4+}}^i {}^0L_{U^{4+},Ce^{4+},O:O}^F)
\end{aligned}
\tag{7}$$

4.5 The M_3O_8 solution phases

Four U_3O_8 polymorphs are described by Guéneau et al.[25, 30] as stoichiometric with respect to oxygen. For this work, CEF models were developed to describe the phases as a solution whereby Ce is accommodated on cation sites using the following sublattice representation:

Only the 5+ and 6+ oxidation states for U are included in this representation based on a recent spectroscopic study [35] showing U^{5+} and U^{6+} to predominate in U_3O_8 . The Gibbs energy of the phase defined with an ideal CEF is then:

$$G^{M_3O_8} = y_{U^{5+}}^i y_{O}^{ii} {}^\circ G_{U^{5+},O}^{M_3O_8} + y_{U^{6+}}^i y_{O}^{ii} {}^\circ G_{U^{6+},O}^{M_3O_8} + y_{Ce^{4+}}^i y_{O}^{ii} {}^\circ G_{Ce^{4+},O}^{M_3O_8} + 3RT \left(y_{U^{5+}}^i \ln y_{U^{5+}}^i + y_{U^{6+}}^i \ln y_{U^{6+}}^i + y_{Ce^{4+}}^i \ln y_{Ce^{4+}}^i \right)
\tag{8}$$

Both ${}^\circ G_{U^{5+},O}^{M_3O_8}$ and ${}^\circ G_{U^{6+},O}^{M_3O_8}$ are taken to be equal to the stoichiometric function used to describe each polymorph in [25] but adjusted by adding $RT(2/3 \ln 2/3 + 1/3 \ln 1/3)$ to each in order to account for the mixing effect in a pure U_3O_8 such that the models are consistent with the current U-O assessment [25]. The Gibbs energy of the Ce containing end-members were first set equal to either ${}^\circ G_{U^{5+},O}^{M_3O_8}$ or ${}^\circ G_{U^{6+},O}^{M_3O_8}$ for the appropriate polymorph with the standard state enthalpies chosen as adjustable parameters.

4.6 Parameter optimization

The Optisage module of FactSage [27] was utilized to find the best fit to μ_{O_2} , C_p , and phase equilibria measurements for the U-Ce-O systems using the models described above. The thermodynamic functions in Table 2 were used along with those for the U-O assessments of Guéneau et al. [25] and McMurray et al. [34]. An iterative procedure was employed to simultaneously optimize all adjustable parameters for all the models in order to achieve a self-consistent set of values that sufficiently describes the thermodynamic behavior of the U-Ce-O system.

5. Results and discussion

5.1 Equilibrium oxygen pressures over $U_{1-y}Ce_yO_{2\pm x}$

The logarithm of the equilibrium oxygen pressures as a function of O/M for $y = 0.0, 0.05, 0.20$, and 0.30 measured by TGA in this work are distinguished by laboratory in Table 3. Compositions corresponding to $y = 0.50$ are not shown since these were inconsistent with the balance of data collected in this work, the studies of Ducroux and Baptiste [5], and Markin and Crouch [9]. Errors were likely introduced in the p_{O_2} vs O/M measurements of $U_{0.50}Ce_{0.50}O_{2-x}$ due to a reaction with the Al_2O_3 crucible; this is discussed in more detail in Section 6.

5.2 Thermochemical data

As mentioned above, both μ_{O_2} and C_p were used to develop the CEF model for $U_{1-y}Ce_yO_{2\pm x}$. Figure 5 shows good agreement between the experimental and computed $\log p_{O_2}$ versus O/M for $U_{1-y}Ce_yO_{2\pm x}$ at varying temperatures. While the μ_{O_2} measurements from Brown [4] were discarded from the optimization because of repeatability issues, the exception were those for $y = 0.50$. These are plotted in Fig. 5c as $\log p_{O_2}$ data where they compare fairly well to the computed values for $U_{1-y}Ce_yO_{2\pm x}$ and those from other studies at the same Ce cation fractions and similar temperatures. However, at $1.85 < O/M < 1.86$, Brown [4] observed a nearly linear μ_{O_2} vs O/M behavior indicative of three phase equilibrium.

Lorenzelli and Touzelin [8] proposed a tri-phasic region (Fig. 1a reproduced as given in [36]) for $U_{0.50}Ce_{0.50}O_{2-x}$ conditioned in an H_2 atmosphere which corresponds with that observation. Due to the limited amount of data found exclusively in [8], this assessment does not include the existence of a three phase field; however, this is a possible explanation for the discrepancy between the calculated μ_{O_2} values from the model and those made by Brown [4]. Figure 6 compares the C_p measurements from Nelson et al. [1], Venkata et al. [37], and Arita et al. [14] to the C_p versus temperature curves computed using the model for $U_{1-y}Ce_yO_{2.00}$. Good agreement is seen with the results of [14] and [1]; however, the data from Venkata et al. [37] are too high and deviate from the trend of decreasing C_p with increasing Ce content. The model for $U_{1-y}Ce_yO_{2\pm x}$ predicts higher C_p values with decreasing O/M; since sealed aluminum crucibles were used in [37], the aluminum likely reduced the mixed oxide sample and introduced error resulting in the atypical results seen in Fig. 6.

5.3 The U-Ce binary phase diagram

Haefling and Dane [38] observed very limited mutual solubilities of U and Ln in the binary systems. Therefore, all condensed phases were assumed to be immiscible as was done for U-Gd [34], U-La [39], U-Y[40], and U-Nd [41]. A tentative diagram of the U-Ce binary is shown in Fig. 7.

5.4 Ternary phase equilibria

Figures 8 – 10 show the calculated phase relations compare well to those determined experimentally using XRD from [6, 8, 16, 17] and melting measurements from [18, 19]. The model for $U_{1-y}Ce_yO_{2\pm x}$ correctly predicts the appearance of a miscibility gap observed by several authors [6, 8, 16] at low temperatures, and the compositional space over which it exists at 873 K, 673 K, and 473 K shows good

agreement with high temperature X-ray diffraction (HTXRD) results from [16]. Nawada et al.[17] report some dissolution of Ce in orthorhombic U_3O_8 with a solubility of 12 at. % at 873 K and between 6.5-10.5 at. % over the 1123-1273 K temperature range. The O/M vs y relationship at 1123 K in air shown in Fig. 8b can be interpreted as follows. From $y = 0.0$ to 0.1 , the O/M maintains a constant value of $8/3$ due to the stability of a single M_3O_8 phase. Above $y = 0.1$, M_3O_8 and $U_{1-y}Ce_yO_{2\pm x}$ coexist. From $y \approx 0.75$ to 1.0 , only the fluorite $U_{1-y}Ce_yO_{2\pm x}$ solution is stable. As can be seen in Fig. 8b, the models from this work well represent the data reported by Nawada et al. [17] and Markin et al. [16] along what can be considered the fully oxidized isopleth. The computed high temperature ternary diagram at 1773 K is given in Fig. 11.

5.4 Cerium as a surrogate in MOX

While Ce and Pu share comparable ionic radii and the same predominant oxidation states, their properties as pure di-oxides differ enough to affect the thermodynamics of compositionally equivalent fluorite solutions with U. For example, the melting point of CeO_2 and PuO_2 are ~ 2500 K [26] and ~ 2353 K [42] respectively. Further, the μ_{O_2} relationship versus temperature and composition for CeO_{2-x} and PuO_{2-x} differ with ceria exhibiting higher μ_{O_2} values. In the Ce-O and Pu-O binaries, Ce forms many more stoichiometric compounds with O than does Pu. Finally, Nelson et al. [1] compared the thermophysical properties of CeO_2 to PuO_2 in [1] and showed and these exhibit significant differences. The Gibbs energies of solutions are based on pure end-member compounds. Thus, the properties of CeO_2 and PuO_2 cause heavily influence and cause differences in the thermodynamic behavior of $U_{1-y}Ce_yO_{2\pm x}$ and $U_{1-y}Pu_yO_{2\pm x}$.

Nelson et al. [1] pointed out that CeO_2 is not a suitable surrogate for PuO_2 if thermal conductivity is the property of interest. This study echoes those findings but from a thermochemical perspective. Figures 12 and 13 illustrate that the $\log p_{O_2}$ and the phase equilibria of $U_{1-y}Ce_yO_{2\pm x}$ and $U_{1-y}Pu_yO_{2\pm x}$ differ more significantly as y increases. That is, the solidus and liquidus temperatures along the UO_2 - CeO_2 isopleth show a reasonable similarity to those of UO_2 - PuO_2 only for small values of y as seen in Fig. 10. Therefore, the thermodynamic suitability of Ce as a surrogate for Pu in MOX is highly dependent on composition, e.g. the O/M and metal fraction of the $U_{1-y}M_yO_{2\pm x}$ phase. Typical Pu contents in MOX is between $0.20 < y < 0.40$, suggesting that the utility of $U_{1-y}Ce_yO_{2\pm x}$ to act as a thermodynamic surrogate for $U_{1-y}Pu_yO_{2\pm x}$ will be limited to the lower end of that range.

5.5 MDD versus solid state sample preparation results

The data between laboratories from Table 3 cannot be compared directly since the measurements were taken at different temperatures and/or compositions. However, the trends are consistent and the CEF model fit to the p_{O_2} is very good. This implies little difference between samples produced using the traditional mechanical mixing technique at LANL and those made via MDD route at ORNL. Consequently, both fabrication approaches can be assumed to produce fully homogenous fluorite urania-ceria solid solutions.

5.6 The $AlCeO_3$ and $Al_{11}CeO_{18}$ phases

Figure 14 shows the computed defect and cation concentrations as a function of $\log p_{O_2}$ and O/M at 1773 K and $y = 0.50$ derived from the CEF model of the phase. At low $\log p_{O_2}$ values, the CEF for $U_{1-y}Ce_yO_{2\pm x}$ predicts that Ce is primarily reduced from 4+ to a 3+ cation state. As mentioned in Section 3.2, an alumina crucible was used to for the TGA measurements. Ceria has been observed to react with Al_2O_3 to form an $AlCeO_3$ compound in reducing atmospheres [43, 44]. Calculations using the Gibbs energies for $AlCeO_3$ and $Al_{11}CeO_{18}$ from the FactSage database along with the models developed in this work predict a reaction between $U_{1-y}Ce_yO_{2\pm x}$ and Al_2O_3 that becomes more significant with increasing y and temperature and decreasing oxygen pressures. Cerium thus combines with Al_2O_3 to form either $AlCeO_3$ (or $Al_{11}CeO_{18}$ at higher temperatures) while U remains in the fluorite $U_{1-y}Ce_yO_{2\pm x}$ solution. Indeed, measurements on $U_{1-y}Ce_yO_{2\pm x}$ for $y > 0.20$ at low oxygen pressures and high temperatures suffered from repeatability issues and had to be discarded likely due to the reaction discussed above.

6. Summary and Conclusions

A thermodynamic assessment of the U-Ce-O system has been performed using the Calphad approach. The CEF model for fluorite urania-ceria compares very well to the experimentally determined oxygen potentials and heat capacities. The calculated phase relations presented in this work agree well with data from XRD and HTXRD studies. However, the ternary phase field reported by Lorenzelli and Touzelin [8] should be the subject of future experimental work. The overall agreement between the computed and observed thermodynamic behavior in the U-Ce-O system is good.

The results from this work allow the thermodynamic behavior of the U-Ce-O and U-Pu-O [42] systems to be directly compared. As concluded in [1], the suitability of Ce as a surrogate for Pu in MOX studies is highly dependent on the fuel form, the composition, and the properties to be measured. Further, this assessment provides an improved understanding of the chemical behavior of the U-O system with Ce, an important FP due to its high-yield. The models presented herein can be combined with those for other U-O containing systems and extended to include additional fission and activation products for a more comprehensive representation of the thermodynamics of high-burnup fuel.

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List of Figures

Figure 1. Phase relations reported by Lorenzelli and Touzelin (a), Hoch and Furman (b), Nawada et al. (c) and Markin et al. (d). Figure (a) is reprinted with permission of The American Ceramic Society, www.ceramics.org. All rights reserved.

Figure 2. Comparison of equilibrium oxygen pressures versus O/M for UO_{2+x} from this work using thermogravimetry to measurements of Aronson and Belle [23] and Lindemer and Sutton [21].

Figure 3. Phase relations in the Ce-O binary computed using the CEF for CeO_{2-x} after Zinkevich et al. [26](a) and the three-sublattice version from this work (b).

Figure 4. A comparison of the CEF predicted equilibrium oxygen pressures (a) and Cp (b) for CeO_{2-x} using the model developed by Zinkevich et al. [26] and the three-sublattice version from this work.

Figure 5. Equilibrium oxygen pressures (symbols) for $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ compared to those computed by the CEF model shown as solid lines (a) for $y = 0.30$, (b) for $y = 0.05$, (c) at high Ce compositions, and (d) for $y = 0.20$ from this work compared to similar compositions determined in separate studies.

Figure 6. Molar heat capacity computed (lines) using the CEF versus those experimentally determined for ostensibly stoichiometric $\text{U}_{1-y}\text{Ce}_y\text{O}_{2.00}$. The long dashed lines and the short dashed lines are for UO_2 and CeO_2 respectively.

Figure 7. Tentative calculated U-Ce binary phase diagram.

Figure 8. (a) Section of the U-Ce-O system in the vicinity of the single phase fluorite solution at 873 K. (b) Computed O/M (line) at 1123 K at an oxygen pressure of 0.21 atm versus experimentally determined values in air at 1123 K (circles) and 100% O_2 at 1173 K (triangles). (F-fluorite solution, O-orthorhombic U_3O_8 , A- Ce_2O_3)

Figure 9. (a) Section of the U-Ce-O system at 473 K and (b) 673 showing a good agreement with the fluorite solution miscibility gap data (filled circles) from Markin et al. [16]. (F-fluorite solution, O-orthorhombic U_3O_8 , A- Ce_2O_3)

Figure 10. Comparison of the melting behavior along the (a) UO_2 - CeO_2 and (b) UO_2 - PuO_2 isopleths. The open circles represent melting measurements from [18] while the open triangle is a solidus and the filled triangle a liquidus determination from [19].

Figure 11. Computed U-Ce-O high-temperature isotherm at 1773 K. (F-fluorite solution, O-orthorhombic U_3O_8 , A- Ce_2O_3 , L1-liquid 1, L2-liquid 2)

Figure 12. Computed equilibrium oxygen pressures as a function of O/M using the CEF for $U_{1-y}Ce_yO_{2\pm x}$ (solid lines) from this work and that for $U_{1-y}Pu_yO_{2\pm x}$ (dashed lines) from [25, 42] at 1273 K for (a) $y = 0.10$, (b) $y = 0.25$, (c) $y = 0.75$, and (d) $y = 0.90$.

Figure 13. Section of the phase relations in the vicinity of the single phase fluorite region for U-Ce-O (a) and U-Pu-O (b) at 1273 K. Compositions corresponding to those from equilibrium oxygen pressure determinations are shown as symbols in (a). (F-fluorite solution, O-orthorhombic U_3O_8 , A- Ce_2O_3)

Figure 14. The CEF computed sublattice site fractions as a function of O/M (a) and $\log p_{O_2}$ (b) at 1773 K for $U_{0.50}Ce_{0.50}O_{2\pm x}$. The tetrahedral and octahedral sublattices are distinguished by the (ii) and (iii) symbols respectively.

Table 1.

Equilibrium oxygen pressure data reported for fluorite $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ solutions.

Authors	Ref.	y	Temperature (K)	$-\log p_{\text{O}_2}$	O/M	Method
Ducroux and Baptiste	[4]	0.34–0.75	873–1273	36.4–14.7	1.923–2.000	EMF
Nagarajan et al.	[9]	0.20–0.50	1073–1173	26.1–18.88	1.944–2.000	WCA
Tagawa et al.	[11]	0.60–0.80	1373	0.7	2.115–2.240	TGA
Blackburn	[12]	0.11	1807	14.7–13.91	1.826–2.000	EMF
Hoch and Furman	[5]	0.15–0.35	1173	12.24–8.38	1.840–2.000	TGA
Lorenzelli and Touzelin	[7]	0.34	1273	24.0–14.1	1.915–2.000	TGA
Norris and Kay	[10]	0.15–0.28	1123	22.81–18.00	1.972–2.000	TGA
Markin and Crouch	[8]	0.10–0.75	1073–1223	23.98–17.53	1.868–2.114	TGA
Kang et al.	[6]	0.040–0.270	1273	13.24–7.18	1.965–2.048	EMF
Brown	[3]	0.10–0.50	1123–1600	29.88–10.67	1.826–2.000	TGA/EMF

WCA – wet chemical analysis technique, EMF – electromotive force, TGA – thermogravimetric analysis

Table 3.

Equilibrium oxygen pressures over $\text{U}_{1-y}\text{Ce}_y\text{O}_{2\pm x}$ using thermogravimetric analysis.

y	Temperature (K)	O/M	$\log p_{\text{O}_2}$	Error in $\log p_{\text{O}_2}$	Laboratory
0.0	1350	2.000	-18	0.079	ORNL
0.0	1350	2.000	-11	0.116	ORNL
0.0	1350	2.002	-10	0.269	ORNL
0.0	1350	2.007	-9	0.806	ORNL
0.0	1350	2.270	-4	0.270	ORNL
0.0	1573	2.000	-15	0.056	ORNL
0.0	1573	2.002	-11	0.288	ORNL
0.0	1573	2.046	-6.6	0.747	ORNL
0.0	1573	2.169	-4	0.262	ORNL
0.05	1073	2.000	-20.90	0.110	ORNL
0.05	1073	2.000	-19.99	0.110	ORNL
0.05	1073	2.000	-20.92	0.110	ORNL
0.05	1073	2.000	-20.17	0.110	ORNL
0.05	1073	2.000	-17.92	0.111	ORNL
0.05	1073	2.000	-15.99	0.138	ORNL
0.05	1073	2.000	-14.99	0.270	ORNL
0.05	1273	1.998	-21.00	0.079	ORNL
0.05	1273	1.998	-20.00	0.079	ORNL
0.05	1273	1.999	-19.00	0.079	ORNL
0.05	1273	1.999	-17.00	0.079	ORNL
0.05	1273	2.000	-17.00	0.079	ORNL
0.05	1273	2.000	-17.00	0.079	ORNL
0.05	1273	2.000	-15.00	0.079	ORNL
0.05	1273	2.000	-16.00	0.079	ORNL
0.05	1273	2.000	-15.00	0.079	ORNL
0.05	1273	2.000	-13.00	0.086	ORNL
0.05	1273	2.000	-13.04	0.086	ORNL
0.05	1523	1.985	-19.47	0.058	ORNL
0.05	1523	1.986	-18.89	0.055	ORNL
0.05	1523	1.997	-13.75	0.055	ORNL
0.05	1523	1.998	-13.00	0.055	ORNL

0.05	1523	1.999	-11.00	0.056	ORNL
0.05	1523	1.999	-10.00	0.060	ORNL
0.05	1523	1.999	-9.00	0.088	ORNL
0.05	1523	2.004	-7.00	0.611	ORNL
0.05	1273	1.971	-19.75	0.079	ORNL
0.20	1073	1.985	-23.99	0.110	ORNL
0.20	1073	1.995	-21.49	0.110	ORNL
0.20	1073	1.999	-19.99	0.110	ORNL
0.20	1073	1.999	-19.00	0.110	ORNL
0.20	1073	2.000	-18.30	0.110	ORNL
0.20	1073	2.000	-16.98	0.114	ORNL
0.20	1073	2.000	-17.60	0.111	ORNL
0.20	1073	2.001	-15.96	0.139	ORNL
0.20	1073	2.001	-16.53	0.120	ORNL
0.20	1073	2.001	-14.53	0.424	ORNL
0.20	1273	1.990	-16.99	0.079	ORNL
0.20	1273	1.994	-16.01	0.079	ORNL
0.20	1273	1.997	-15.00	0.079	ORNL
0.20	1273	1.999	-14.00	0.080	ORNL
0.20	1273	1.999	-13.00	0.086	ORNL
0.20	1273	1.999	-13.00	0.086	ORNL
0.20	1273	2.000	-12.00	0.128	ORNL
0.20	1273	2.000	-11.00	0.313	ORNL
0.20	1273	2.000	-10.69	0.433	ORNL
0.20	1273	2.001	-10.00	0.897	ORNL
0.20	1473	1.991	-14.27	0.079	LANL
0.20	1473	1.985	-15.18	0.079	LANL
0.20	1473	1.991	-14.40	0.079	LANL
0.20	1473	1.986	-15.07	0.079	LANL
0.20	1473	1.990	-14.62	0.079	LANL
0.20	1473	1.987	-14.94	0.079	LANL
0.20	1473	1.988	-14.80	0.079	LANL
0.20	1473	1.993	-14.28	0.079	LANL
0.20	1473	1.999	-11.99	0.079	LANL

0.20	1473	1.999	-12.50	0.079	LANL
0.20	1473	2.000	-10.90	0.081	LANL
0.20	1473	1.998	-12.96	0.079	LANL
0.20	1473	1.999	-11.97	0.079	LANL
0.20	1473	1.997	-13.37	0.079	LANL
0.20	1473	1.993	-14.22	0.079	LANL
0.20	1473	1.983	-15.22	0.079	LANL
0.20	1473	1.987	-14.74	0.079	LANL
0.20	1473	1.992	-14.03	0.079	LANL
0.20	1473	1.994	-13.74	0.079	LANL
0.20	1473	2.000	-10.88	0.081	LANL
0.20	1473	2.000	-10.08	0.088	LANL
0.20	1473	2.000	-9.44	0.112	LANL
0.20	1473	2.000	-9.12	0.137	LANL
0.20	1473	2.000	-8.83	0.173	LANL
0.20	1673	1.994	-11.28	0.055	LANL
0.20	1673	1.999	-10.28	0.056	LANL
0.20	1673	1.993	-11.55	0.055	LANL
0.20	1673	2.000	-9.07	0.057	LANL
0.20	1673	1.995	-10.97	0.055	LANL
0.20	1673	1.987	-12.03	0.055	LANL
0.20	1673	2.000	-9.06	0.057	LANL
0.20	1673	1.970	-13.12	0.055	LANL
0.20	1673	1.977	-12.47	0.055	LANL
0.20	1673	1.980	-12.21	0.055	LANL
0.20	1673	1.989	-11.31	0.055	LANL
0.20	1673	1.997	-9.92	0.056	LANL
0.20	1673	1.999	-8.99	0.057	LANL
0.20	1673	2.000	-8.00	0.067	LANL
0.20	1673	2.000	-7.15	0.110	LANL
0.20	1673	2.000	-6.87	0.140	LANL
0.20	1673	2.001	-6.64	0.175	LANL
0.20	1873	1.963	-11.43	0.041	LANL
0.20	1873	1.973	-10.57	0.041	LANL

0.20	1873	1.978	-10.15	0.041	LANL
0.20	1873	1.991	-8.92	0.041	LANL
0.20	1873	1.996	-8.12	0.042	LANL
0.20	1873	1.998	-7.61	0.043	LANL
0.20	1873	1.999	-7.39	0.043	LANL
0.20	1873	1.999	-7.11	0.045	LANL
0.30	1473	1.998	-10.96	0.080	LANL
0.30	1473	1.999	-10.43	0.084	LANL
0.30	1473	1.998	-11.28	0.080	LANL
0.30	1473	1.999	-10.42	0.084	LANL
0.30	1473	1.996	-11.72	0.079	LANL
0.30	1473	1.999	-10.40	0.084	LANL
0.30	1473	1.996	-11.70	0.079	LANL
0.30	1473	1.995	-12.01	0.079	LANL
0.30	1473	1.996	-11.72	0.079	LANL
0.30	1473	1.993	-12.30	0.079	LANL
0.30	1473	1.996	-11.73	0.079	LANL
0.30	1473	1.991	-12.53	0.079	LANL
0.30	1473	1.995	-11.72	0.079	LANL
0.30	1473	1.991	-12.50	0.079	LANL
0.30	1473	1.968	-14.58	0.079	LANL
0.30	1473	1.991	-12.53	0.079	LANL
0.30	1473	1.968	-14.59	0.079	LANL
0.30	1473	1.999	-10.44	0.084	LANL
0.30	1473	1.959	-15.15	0.079	LANL
0.30	1473	1.977	-13.80	0.079	LANL
0.30	1473	1.987	-12.93	0.079	LANL
0.30	1473	1.997	-11.35	0.080	LANL
0.30	1473	1.999	-10.48	0.083	LANL
0.30	1473	1.999	-10.22	0.086	LANL
0.30	1473	2.000	-8.99	0.152	LANL
0.30	1473	2.000	-8.71	0.194	LANL
0.30	1473	2.000	-8.45	0.250	LANL
0.30	1673	1.999	-9.06	0.057	LANL

0.30	1673	1.990	-10.38	0.055	LANL
0.30	1673	1.996	-9.63	0.056	LANL
0.30	1673	1.997	-9.40	0.056	LANL
0.30	1673	1.995	-9.84	0.056	LANL
0.30	1673	1.997	-9.42	0.056	LANL
0.30	1673	1.993	-10.06	0.056	LANL
0.30	1673	1.992	-10.26	0.056	LANL
0.30	1673	1.990	-10.51	0.055	LANL
0.30	1673	1.980	-11.24	0.055	LANL
0.30	1673	1.952	-12.88	0.055	LANL
0.30	1673	1.993	-10.31	0.055	LANL
0.30	1673	1.945	-13.11	0.055	LANL
0.30	1673	1.963	-11.84	0.055	LANL
0.30	1673	1.970	-11.38	0.055	LANL
0.30	1673	1.988	-10.02	0.056	LANL
0.30	1673	1.998	-8.37	0.061	LANL
0.30	1673	1.998	-8.09	0.066	LANL
0.30	1673	1.999	-7.78	0.074	LANL
0.30	1673	2.000	-7.41	0.091	LANL
0.30	1673	2.000	-7.13	0.112	LANL
0.30	1673	2.000	-6.87	0.141	LANL
0.30	1673	2.001	-6.56	0.191	LANL
0.30	1873	1.956	-10.02	0.041	LANL
0.30	1873	1.982	-8.37	0.041	LANL
0.30	1873	1.991	-7.58	0.043	LANL
0.30	1873	1.998	-6.62	0.050	LANL

Table 2.

Gibbs functions for the models constituting the U-Ce-O assessment.

Thermodynamic parameters (J/mole)	Reference
Gas phase	
$^{\circ}G_{O_2}^{gas}$	[28]
$^{\circ}G_{O_3}^{gas}$	[28]
$^{\circ}G_O^{gas}$	[28]
$^{\circ}G_{Ce}^{gas}$	[28]
$^{\circ}G_{Ce_2}^{gas}$	[28]
$^{\circ}G_{CeO}^{gas}$	[28]
$^{\circ}G_{CeO_2}^{gas}$	[28]
$^{\circ}G_U^{gas}$	[29]
$^{\circ}G_{UO_3}^{gas}$	[29]
$^{\circ}G_{UO_2}^{gas}$	[29]
$^{\circ}G_{UO}^{gas}$	[29]
Pure elements and stoichiometric compounds	
$^{\circ}G_U^{\alpha}$	[28]
$^{\circ}G_U^{\beta}$	[28]
$^{\circ}G_U^{\gamma}$	[28]
$^{\circ}G_{UO_3}^{solid}$	[25]
$^{\circ}G_{U_3O_8}^{\alpha}$	[25]
$^{\circ}G_{U_3O_8}^{\beta}$	[25]
$^{\circ}G_{U_3O_8}^{\gamma}$	[25]
$^{\circ}G_{U_3O_8}^{\delta}$	[25]
$^{\circ}G_{U_4O_9}^{\alpha}$	[25]
$^{\circ}G_{U_4O_9}^{\beta}$	[25]
$^{\circ}G_{U_4O_9}^{\gamma}$	[25]
$^{\circ}G_{Ce_7O_{12}}$	[26]
$^{\circ}G_{Ce_9O_{16}}$	[26]
$^{\circ}G_{Ce_{11}O_{20}}$	[26]

$$^{\circ}G_{Ce_{19}O_{34}} \quad [26]$$

$$^{\circ}G_{Ce_{40}O_{72}} \quad [26]$$

$$^{\circ}G_{Ce_{62}O_{112}} \quad [26]$$

Fluorite solution ($U^{3+}, U^{4+}, U^{5+}, U^{6+}, Ce^{3+}, Ce^{4+}$)₁(O^{2-}, Va^0)₂(O^{2-}, Va^0)

$$^{\circ}G_{UO_2}^F \quad [28]$$

$$^{\circ}G_{CeO_2}^F \quad [26]$$

$$^{\circ}G_{Ce_2O_3}^F \quad [26]$$

$$^{\circ}G_{U^{3+};O^{2-};O^{2-}}^F = ^{\circ}G_{U^{3+};O^{2-};Va}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [25]$$

$$^{\circ}G_{U^{3+};O^{2-};Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{U^{4+};Va;Va}^F + ^{\circ}G_{U^{3+};Va;Va}^F \quad [25]$$

$$^{\circ}G_{U^{3+};Va;Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{O_2}^{gas} + 747127 - 70.23 T - 2 RT [0.75 \ln(0.75) + 0.25 \ln(0.25)] \quad [25]$$

$$^{\circ}G_{U^{3+};Va;O^{2-}}^F = 100000 \quad [25]$$

$$^{\circ}G_{U^{4+};O^{2-};O^{2-}}^F = ^{\circ}G_{UO_2}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [25]$$

$$^{\circ}G_{U^{4+};O^{2-};Va}^F = ^{\circ}G_{UO_2}^F \quad [25]$$

$$^{\circ}G_{U^{4+};Va;Va}^F = ^{\circ}G_{UO_2}^F - ^{\circ}G_{O_2}^{gas} + 545210.5 \quad [25]$$

$$^{\circ}G_{U^{4+};Va;O^{2-}}^F = 100000 \quad [25]$$

$$^{\circ}G_{U^{5+};O^{2-};O^{2-}}^F = ^{\circ}G_{U^{5+};O^{2-};Va}^F + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [25]$$

$$^{\circ}G_{U^{5+};O^{2-};Va}^F = ^{\circ}G_{UO_2}^F - 58351.62 + 39.68 T - RT \ln(0.5) \quad [25]$$

$$^{\circ}G_{U^{5+};Va;Va}^F = ^{\circ}G_{U^{5+};O^{2-};Va}^F - ^{\circ}G_{O_2}^{gas} + 700000 \quad [25]$$

$$^{\circ}G_{U^{5+};Va;O^{2-}}^F = 100000 \quad [25]$$

$$^{\circ}G_{U^{6+};O^{2-};O^{2-}}^F = ^{\circ}G_{U^{5+};O^{2-};O^{2-}}^F + 31961.2 + 0.498 T \quad [34]$$

$$^{\circ}G_{U^{6+};O^{2-};Va}^F = ^{\circ}G_{U^{5+};O^{2-};Va}^F + 31961.3 + 0.978 T \quad [34]$$

$$^{\circ}G_{U^{6+};Va;Va}^F = ^{\circ}G_{U^{5+};Va;Va}^F - 668038.4 - 2.062 T \quad [34]$$

$$^{\circ}G_{U^{6+};Va;O^{2-}}^F = 100000 \quad [34]$$

$$^{\circ}G_{Ce^{3+};O^{2-};Va}^F = ^{\circ}G_{Ce_2O_3}^F + \frac{1}{2}^{\circ}G_{O_2} + 18.702165 T \quad [26]$$

$$^{\circ}G_{Ce^{3+};O^{2-};O^{2-}}^F = ^{\circ}G_{Ce^{3+};O^{2-};Va}^F + \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^{\circ}G_{Ce^{3+};Va;Va}^F = ^{\circ}G_{Ce_2O_3}^F - \frac{1}{2}^{\circ}G_{O_2} + 18.702165 T \quad [26]$$

$$^{\circ}G_{Ce^{3+};Va;O^{2-}}^F = ^{\circ}G_{Ce^{3+};Va;Va}^F - \frac{1}{2}^{\circ}G_{O_2} \quad \text{This work}$$

$$^{\circ}G_{Ce^{4+};O^{2-};O^{2-}}^F = ^{\circ}G_{CeO_2}^F + \frac{1}{2}^{\circ}G_{O_2}$$

This work

$$^{\circ}G_{Ce^{4+};O^{2-};Va}^F = ^{\circ}G_{CeO_2}^F \quad [26]$$

$$^{\circ}G_{Ce^{4+};Va;Va}^F = ^{\circ}G_{CeO_2}^F - ^{\circ}G_{O_2} \quad [26]$$

$$^{\circ}G_{Ce^{4+};Va;O^{2-}}^F = ^{\circ}G_{Ce^{4+};Va;Va}^F - \frac{1}{2}^{\circ}G_{O_2}$$

This work

$$^FL_{U^{4+};U^{5+};O^{2-};O^{2-}}^0 = -124936 - 21.68 \text{ T} \quad [25]$$

$$^FL_{U^{3+};U^{4+};O^{2-};Va}^0 = 40133.7 \quad [25]$$

$$^FL_{U^{3+};U^{4+};O^{2-};Va}^1 = 1076.4 \quad [25]$$

$$^FL_{Ce^{3+};Ce^{4+};O^{2-};Va}^0 = ^FL_{Ce^{3+};Ce^{4+};Va;Va}^0 = -58786 + 12.98725 \text{ T} \quad [26]$$

$$^FL_{Ce^{3+};Ce^{4+};O^{2-};Va}^1 = ^FL_{Ce^{3+};Ce^{4+};Va;Va}^1 = -57516.5 + 15.5513 \text{ T} \quad [26]$$

$$^FL_{U^{4+};Ce^{3+};O^{2-};Va}^0 = -150000 \quad \text{This work}$$

$$^FL_{U^{4+};Ce^{3+};Va;Va}^0 = -300000 \quad \text{This work}$$

$$^FL_{U^{4+};Ce^{4+};Va;Va}^0 = -200000 \quad \text{This work}$$

$$^FL_{U^{4+};Ce^{3+};Va;Va}^1 = ^FL_{U^{4+};Ce^{4+};Va;Va}^1 = -105000 \quad \text{This work}$$

$$^FL_{U^{4+};Ce^{4+};O^{2-};Va}^0 = 25000 - 40 \text{ T} \quad \text{This work}$$

$$^FL_{U^{5+};Ce^{4+};O^{2-};O^{2-}}^0 = ^FL_{U^{5+};Ce^{4+};O^{2-};Va}^0 = -80000 \quad \text{This work}$$

$$^FL_{U^{5+};Ce^{4+};Va;Va}^0 = -199980 \quad \text{This work}$$

α -M₃O₈ (U⁵⁺,U⁶⁺,Ce⁴⁺)₃(O²⁻)₈

$$^{\circ}G_{U^{5+};O^{2-}}^{\alpha} = ^{\circ}G_{U_3O_8}^{\alpha} + 3RT \left(2/3 \ln 1/3 + 1/3 \ln 1/3 \right) \quad \text{This work}$$

$$^{\circ}G_{U^{6+};O^{2-}}^{\alpha} = ^{\circ}G_{U^{5+};O^{2-}}^{\alpha} \quad \text{This work}$$

$$^{\circ}G_{Ce^{4+};O^{2-}}^{\alpha} = ^{\circ}G_{U^{5+};O^{2-}}^{\alpha} + 220000 \quad \text{This work}$$

β -M₃O₈ (U⁵⁺,U⁶⁺,Ce⁴⁺)₃(O²⁻)₈

$$^{\circ}G_{U^{5+};O^{2-}}^{\beta} = ^{\circ}G_{U_3O_8}^{\beta} + 3RT \left(2/3 \ln 1/3 + 1/3 \ln 1/3 \right) \quad \text{This work}$$

$$^{\circ}G_{U^{6+};O^{2-}}^{\beta} = ^{\circ}G_{U^{5+};O^{2-}}^{\beta} \quad \text{This work}$$

$$^{\circ}G_{Ce^{4+};O^{2-}}^{\beta} = ^{\circ}G_{U^{5+};O^{2-}}^{\beta} + 220000 \quad \text{This work}$$

γ -M₃O₈ (U⁵⁺,U⁶⁺,Ce⁴⁺)₃(O²⁻)₈

$$^{\circ}G_{U^{5+};O^{2-}}^{\gamma} = ^{\circ}G_{U_3O_8}^{\gamma} + 3RT \left(2/3 \ln 1/3 + 1/3 \ln 1/3 \right)$$

This work

$$^{\circ}G_{U^{6+};O^{2-}}^{\gamma} = ^{\circ}G_{U^{5+};O^{2-}}^{\gamma}$$

This work

$$^{\circ}G_{Ce^{4+};O^{2-}}^{\gamma} = ^{\circ}G_{U^{5+};O^{2-}}^{\gamma} + 220000$$

This work

$$^{\circ}G_{U^{5+};O^{2-}}^{\delta} = ^{\circ}G_{U_3O_8}^{\delta} + 3RT \left(2/3 \ln 1/3 + 1/3 \ln 1/3 \right)$$

This work

$$^{\circ}G_{U^{6+};O^{2-}}^{\delta} = ^{\circ}G_{U^{5+};O^{2-}}^{\delta}$$

This work

$$^{\circ}G_{Ce^{4+};O^{2-}}^{\delta} = ^{\circ}G_{U^{5+};O^{2-}}^{\delta} + 220000$$

This work

$$^{\circ}G_U^{liq} \quad [28]$$

$$^{\circ}G_O^{liq} \quad [25]$$

$$^{\circ}G_{Ce}^{liq} \quad [26]$$

$$^{\circ}G_{UO_2}^{liq} \quad [25]$$

$$^{\circ}G_{CeO_2}^{liq} \quad [26]$$

$$^{\circ}G_{Ce_2O_3}^{liq} \quad [26]$$

$$^{\circ}G_{U^{4+};O^{2-}}^{liq} = ^{\circ}G_{UO_2}^{liq} \quad [25]$$

$$^{\circ}G_{U^{4+};Va}^{liq} = ^{\circ}G_U^{liq} \quad [25]$$

$$^{\circ}G_{Ce^{3+};Va}^{liq} = ^{\circ}G_{Ce}^{liq} \quad [26]$$

$$^{\circ}G_{Ce^{3+};O^{2-}}^{liq} = ^{\circ}G_{Ce_2O_3}^{liq} \quad [26]$$

$$^{\circ}G_{Ce^{4+};Va}^{liq} = 2^{\circ}G_{Ce}^{liq} + 3^{\circ}G_{CeO_2}^{liq} - 2^{\circ}G_{Ce_2O_3}^{liq} \quad [26]$$

$$^{\circ}G_{Ce^{4+};O^{2-}}^{liq} = ^{\circ}G_{CeO_2}^{liq} \quad [26]$$

$$^{liq}L_{U^{4+}.Ce^{3+}.Va}^0 = 1.0E + 6 \quad \text{This work}$$

$$^{liq}L_{U^{4+}.Ce^{4+}.Va}^0 = 1.0E + 6 \quad \text{This work}$$

$$^{liq}L_{U^{4+};O^{2-}.Va}^0 = 1773475.9 - 516T \quad [25]$$

$$^{liq}L_{U^{4+};O^{2-}.Va}^1 = 46774.9 - 120.3789T \quad [25]$$

$$^{liq}L_{U^{4+};O^{2-}.Va}^2 = -500000 \quad [25]$$

$$^{liq}L_{U^{4+};O^{2-}.O^{2-}}^0 = -370000 \quad [25]$$

$${}^{liq}L_{Ce^{3+}.Ce^{4+}:O^{2-}}^0 = -105398 \quad [26]$$

$${}^{liq}L_{Ce^{3+}.Ce^{4+}:O^{2-}}^1 = -35158 \quad [26]$$

$${}^{liq}L_{Ce^{3+}:O^{2-}.Va}^0 = 114250 \quad [26]$$

$${}^{liq}L_{Ce^{4+}.U^{4+}:O^{2-}}^0 = -105000 - 35\,T \quad \text{This work}$$

$${}^{liq}L_{Ce^{3+}.U^{4+}:O^{2-}}^0 = -10000 - 12.5\,T \quad \text{This work}$$

fcc-Ce: (Ce)₁(Va,O)₁

$${}^\circ G_{Ce}^{fcc} \quad [28]$$

$${}^\circ G_{Ce:Va}^{fcc} = {}^\circ G_{Ce}^{fcc} \quad [26]$$

$${}^\circ G_{Ce:O}^{fcc} = {}^\circ G_{Ce}^{fcc} - 525009 + 67.7626\,T + \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

bcc-Ce: (Ce)₁(Va,O)₁

$${}^\circ G_{Ce}^{bcc} \quad [28]$$

$${}^\circ G_{Ce:Va}^{bcc} = {}^\circ G_{Ce}^{bcc} \quad [26]$$

$${}^\circ G_{Ce:O}^{bcc} = {}^\circ G_{Ce}^{bcc} - 521242 + 67.7626\,T + \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

A-Ce₂O₃(Ce²⁺,Ce³⁺)₂(O²⁻,Va⁰)₂(O²⁻,Va⁰)₁

$${}^\circ G_{Ce_2O_3}^A \quad [31]$$

$${}^\circ G_{Ce^{2+}:O^{2-}.Va}^A = \frac{2}{3}{}^\circ G_{Ce_2O_3}^A + \frac{2}{3}{}^\circ G_{Ce}^{fcc} \quad [26]$$

$${}^\circ G_{Ce^{2+}:O^{2-}:O^{2-}}^A = {}^\circ G_{Ce^{2+}:O:Va}^A + \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

$${}^\circ G_{Ce^{3+}:O^{2-}:O^{2-}}^A = {}^\circ G_{Ce_2O_3}^A \quad [26]$$

$${}^\circ G_{Ce^{3+}:O^{2-}.Va}^A = {}^\circ G_{Ce_2O_3}^A - \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

$${}^A L_{Ce^{3+}.Ce^{2+}:O^{2-}:O^{2-}}^0 = {}^A L_{Ce^{3+}.Ce^{2+}:O^{2-}.Va}^0 = 102206 \quad [26]$$

H-Ce₂O₃(Ce²⁺,Ce³⁺)₂(O²⁻,Va⁰)₂(O²⁻,Va⁰)₁

$${}^\circ G_{Ce_2O_3}^H \quad [31]$$

$${}^\circ G_{Ce^{2+}:O^{2-}.Va}^H = {}^\circ G_{Ce^{2+}:O^{2-}.Va}^A \quad [26]$$

$${}^\circ G_{Ce^{2+}:O^{2-}:O^{2-}}^H = {}^\circ G_{Ce^{2+}:O:Va}^H + \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

$${}^\circ G_{Ce^{3+}:O^{2-}:O^{2-}}^H = {}^\circ G_{Ce_2O_3}^H \quad [26]$$

$${}^\circ G_{Ce^{3+}:O^{2-}.Va}^H = {}^\circ G_{Ce_2O_3}^H - \frac{1}{2}{}^\circ G_{O_2}^{gas} \quad [26]$$

$${}^H L_{Ce^{3+}.Ce^{2+}:O^{2-}:O^{2-}}^0 = {}^H L_{Ce^{3+}.Ce^{2+}:O^{2-}.Va}^0 = 102206 \quad [26]$$

$$^{\circ}G_{Ce_2O_3}^X \quad [31]$$

$$^{\circ}G_{Ce^{2+};O^{2-};Va}^X = ^{\circ}G_{Ce^{2+};O^{2-};Va}^A \quad [26]$$

$$^{\circ}G_{Ce^{2+};O^{2-};O^{2-}}^X = ^{\circ}G_{Ce^{2+};O^{2-};Va}^X + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [26]$$

$$^{\circ}G_{Ce^{3+};O^{2-};O^{2-}}^X = ^{\circ}G_{Ce_2O_3}^X \quad [26]$$

$$^{\circ}G_{Ce^{3+};O^{2-};Va}^X = ^{\circ}G_{Ce_2O_3}^X - \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [26]$$

$$^XL_{Ce^{3+};Ce^{2+};O^{2-};O^{2-}}^0 = ^XL_{Ce^{3+};Ce^{2+};O^{2-};Va}^0 = 102206 \quad [26]$$

$$^{\circ}G_{Ce_2O_3}^C \quad [31]$$

$$^{\circ}G_{Ce^{3+};O^{2-};Va}^C = ^{\circ}G_{Ce_2O_3}^C \quad [26]$$

$$^{\circ}G_{Ce^{3+};O^{2-};O^{2-}}^C = ^{\circ}G_{Ce_2O_3}^C + \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [26]$$

$$^{\circ}G_{Ce^{4+};O^{2-};Va}^C = 19140 + 2^{\circ}G_{Ce_2O_3}^C - \frac{1}{2}^{\circ}G_{O_2}^{gas} \quad [26]$$

$$^{\circ}G_{Ce^{4+};O^{2-};O^{2-}}^C = 19140 + 2^{\circ}G_{Ce_2O_3}^C \quad [26]$$

$$^CL_{Ce^{3+};Ce^{2+};O^{2-};O^{2-}}^0 = ^CL_{Ce^{3+};Ce^{2+};O^{2-};Va}^0 = -7178 - 17.7264 \text{ } T \quad [26]$$

$$^CL_{Ce^{3+};Ce^{2+};O^{2-};O^{2-}}^1 = ^CL_{Ce^{3+};Ce^{2+};O^{2-};Va}^1 = -25591 + 22.2801 \text{ } T \quad [26]$$

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14