

## Research Article

# Estimating Free Energies of Formation of Titanate ( $M_2Ti_2O_7$ ) and Zirconate ( $M_2Zr_2O_7$ ) Pyrochlore Phases of Trivalent Lanthanides and Actinides

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A linear free energy relationship was developed to predict the Gibbs free energies of formation ( $\Delta G_{f,MvX}^0$ , in kJ/mol) of crystalline titanate ( $M_2Ti_2O_7$ ) and zirconate ( $M_2Zr_2O_7$ ) pyrochlore families of trivalent lanthanides and actinides ( $M^{3+}$ ) from the Shannon-Prewitt radius of  $M^{3+}$  in a given coordination state ( $r_{M^{3+}}$ , in nm) and the nonsolvation contribution to the Gibbs free energy of formation of the aqueous  $M^{3+}$  ( $\Delta G_{n,M^{3+}}^0$ ). The linear free energy relationship for  $M_2Ti_2O_7$  is expressed as  $\Delta G_{f,MvX}^0 = 0.084r_{M^{3+}} + 82.30\Delta G_{n,M^{3+}}^0 - 3640$ . The linear free energy relationship for  $M_2Zr_2O_7$  is expressed as  $\Delta G_{f,MvX}^0 = 0.083r_{M^{3+}} + 83.13\Delta G_{n,M^{3+}}^0 - 3920$ . Estimated free energies were within 0.73 percent of those calculated from the first principles for  $M_2Ti_2O_7$  and within 0.50 percent for  $M_2Zr_2O_7$ . Entropies of formation were estimated from constituent oxides (J/mol), based on an empirical parameter defined as the difference between the measured entropies of formation of the oxides and the measured entropies of formation of the aqueous cation.

## 1. Introduction

Pyrochlore is a mineral that preferentially incorporates large amount of Pu, U (up to 30 wt%), and Th (up to 9 wt%) into its structure [1–4]. Pyrochlores exist as large polyhedra with coordination numbers ranging from 7 to 8, which provides them with the ability to accommodate a wide range of radionuclide (e.g., Pu, U, Ba, Sr, etc.) as well as neutron poisons (e.g., Hf, Gd) [5]. As a result, pyrochlore structure is the primary consideration as immobilization barriers for utilization of excess weapons-grade plutonium and other radioactive elements [6–8]. Due to their high radiation tolerance, pyrochlores are largely used as combined inert matrix fuel forms and waste forms for the “burning” and final disposal of Pu and the minor actinides [8]. Rare earth (RE, also known as lanthanides) titanate pyrochlore ( $RE_2Ti_2O_7$ , where RE = Lu to Sm, or Y) materials have potential use as solid electrolytes and mixed

ionic/electronic conducting electrodes [9], catalysts [5], and ferroelectric/dielectric device components [10–13].

In actual waste forms, due to the presence of several trivalent cations, the pure as well as solid solution phases of pyrochlores of RE with stoichiometry of  $A_2Ti_2O_7$  and  $A_2Zr_2O_7$  such as  $La_2Ti_2O_7$  to  $Lu_2Ti_2O_7$ ,  $La_2Zr_2O_7$  to  $Lu_2Zr_2O_7$  as well as trivalent actinide bearing phases are expected to occur, and their thermodynamic properties are needed to assess the behavior of Synroc-based waste forms and to optimize Synroc fabrications.  $Gd_2Ti_2O_7$  and  $CaZrTi_2O_7$  doped with 3 wt% of  $^{244}Cm$  have been reported [14]. The  $Gd_2Ti_2O_7$  phase and the more general RE titanate pyrochlore formulation ( $RE_2Ti_2O_7$ ) have been reported in both glass and glass-ceramic nuclear waste forms [15, 16].

Actinides (3+, 4+, and 5+) are predicted to form the pyrochlore structure by substitutions on both the A and B sites [17]. Only the largest of the actinides exist in nature and the others must be obtained synthetically, and such processes

may yield only a few atoms of product. As the atomic number increases, the stability of the tripositive state of actinides increases and parallels with the RE that the known properties of the latter can be used to predict quite exactly the properties of the comparable actinides including their free energies of formation. Despite the broad interest in titanate ( $A_2Ti_2O_7$ ) and zircon bearing ( $A_2Zr_2O_7$ ) pyrochlores of RE and actinides, thermodynamic data for pure as well as fictitious pyrochlores and zirconolites of RE and actinides are limited except for the recent measurements of the Gibbs free energy of formation for  $CaZrTi_2O_7$  and  $CaHfTi_2O_7$  phases [18, 19] and the formation enthalpies of the zirconate [20] and titanate pyrochlores [21].

In this study a linear free energy relationship was developed and used to estimate the free energies of formation of trivalent actinide and RE titanate and zirconate pyrochlore phases using the existing thermodynamic data. The free energy relationship is useful in estimating the thermodynamic properties of pure and fictitious phases required for the immobilization reaction construction of solid solution models for actual crystalline phases of pyrochlores.

## 2. The Rare Earth and Actinide Pyrochlore Structure

The natural mineral pyrochlore ( $(Ca, Na)_2Nb_2O_6F$ ) has a large number of both natural and synthetic analogs [15]. The most extended group of synthetic pyrochlores to this date are oxides with the formula  $A_2B_2O_7$ , where A and B are di- and pentavalent or tri- and tetravalent elements, respectively [15].  $RE_2Ti_2O_7$  pyrochlores have been widely studied [22, 23]. Among typical representatives of this group are gadolinium titanate  $Gd_2Ti_2O_7$  and calcium uranium titanate  $CaUTi_2O_7$ , the ceramics selected in the United States for immobilization of Pu and other radioactive elements. The actinide (An) titanate pyrochlores (e.g., actinium titanate pyrochlore,  $Ac_2Ti_2O_7$ ), are closely related in chemical and structural properties to the rare earth titanate pyrochlores (e.g., lanthanum titanate pyrochlore,  $La_2Ti_2O_7$ ).

In the  $A_2B_2O_7$  pyrochlore-type structure the A site is usually occupied by large cations such as lanthanides (Ln), whereas smaller first- or second-row transition elements fit the B site better. The most stable pyrochlore structure is formed when the RE cation is combined with a diamagnetic  $B^{4+}$  cation. In an  $A_2^{3+}B_2^{4+}O_7$  pyrochlore formula, the choice of  $B^{4+}$  cation is thus limited to  $Ti^{4+}$  and  $Sn^{4+}$  and marginally  $Zr^{4+}$  or  $Ge^{4+}$ . RE-zirconate pyrochlores ( $A_2B_2O_7$ , where the B site cation is  $Zr^{4+}$ ) from La to Sm and RE-titanate pyrochlores ( $A_2B_2O_7$ , where the B site cation is  $Ti^{4+}$ ) from Sm to Lu with the coordination of the RE cation of eight and the coordination of Zr and Ti of six have been identified [21]. The fictitious phases of RE-pyrochlores can be expected to form across the entire trivalent RE and actinide series.

## 3. Theoretical Basis of the Free Energy Model

Directly analogous to the well-established Hammett linear free energy relationship for substituted aqueous organic

species and reactions [24–26], Sverjensky and Molling [27], and Sverjensky [28] developed a linear free energy relationship to correlate the standard Gibbs free energies of formation of an isostructural family of crystalline phases to those of aqueous cations of a given charge. For the trivalent RE and actinide isostructural family, the chemical formula of solids may be represented as  $M_vX$ , where M is the trivalent cation ( $M^{3+}$ ) and X represents the remainder of the composition of solid, for instance, in  $M_2(CO_3)_3$ , the trivalent cation M is La, Ce, Pu, and so forth, and X is  $CO_3^{2-}$ ; in RE-zirconate pyrochlore family, the trivalent M is La, Sm, Lu, and so forth and X is  $(Zr_2O_7)^{2-}$ . The original Sverjensky-Molling linear free energy correlation was modified by the authors for trivalent cations as [29]

$$\Delta G_{f,M_vX}^0 = a_{M_vX} \Delta G_{n,M^{3+}}^0 + b_{M_vX} + \beta_{M_vX} r_{M^{3+}}. \quad (1)$$

In (1) the coefficients  $a_{M_vX}$ ,  $b_{M_vX}$  and  $\beta_{M_vX}$ , are characteristic of the particular crystal structure represented by  $M_vX$ , and  $r_{M^{3+}}$  is the Shannon-Prewitt radius of the  $M^{3+}$  cation in a given coordination state [27].  $\beta_{M_vX}$  is a coefficient related to the coordination number (CN) of the cation. In polymorphs, the structure family with smaller CN has higher value of  $\beta_{M_vX}$  than the family with higher CN [27]. The parameter  $\Delta G_{f,M_vX}^0$  is the standard state Gibbs free energies of formation of the end member solids, and the parameter  $\Delta G_{n,M^{3+}}^0$  is the standard state Gibbs free energies of nonsolvation, based on a radius-based correction to the standard state Gibbs free energies of formation ( $\Delta G_{f,M^{3+}}^0$ ) of the aqueous cation,  $M^{3+}$ . The  $\Delta G_{n,M^{3+}}^0$ , not the  $\Delta G_{s,M^{3+}}^0$  or the  $\Delta G_{f,M^{3+}}^0$ , of the cations directly contributes to  $\Delta G_{f,M_vX}^0$  containing the cation ( $M^{3+}$ ). The  $\Delta G_{n,M^{3+}}^0$  and  $\Delta G_{s,M^{3+}}^0$  can be separated from  $\Delta G_{f,M^{3+}}^0$  as follows [27]:

$$\Delta G_{f,M^{3+}}^0 = \Delta G_{n,M^{3+}}^0 + \Delta G_{s,M^{3+}}^0. \quad (2)$$

Equation (1) was rearranged as

$$\Delta G_{f,M_vX}^0 - \beta_{M_vX} r_{M^{3+}} = a_{M_vX} \Delta G_{n,M^{3+}}^0 + b_{M_vX}. \quad (3)$$

The coefficients  $a_{M_vX}$ ,  $b_{M_vX}$ , and  $\beta_{M_vX}$  can be determined by regression if the Gibbs free energies of formation of three or more phases in one isostructural family are known.

## 4. Application of the Free Energy Model to Titanate and Zirconate Pyrochlore Phases

Following the procedure of Sverjensky and Molling we have developed linear free energy correlations for oxide [29] hydroxide [29] carbonate [30], and sulfate isostructural families of trivalent lanthanides and actinides (Table 1). The discrepancies between the calculated and measured data were found to be less than  $\pm 3.0\%$  for all isostructural families (oxides, hydroxides, carbonates, and sulfates).

Based on our results and results from other crystal families, the coefficient  $a_{M_vX}$  or the slope of (3) is only related to the stoichiometry of the solids. The slopes for all polymorphs of composition  $M_vX$  are the same within

TABLE 1: Summary of regression analysis: Gibbs free energies of formation of bulk solids of trivalent lanthanides and actinides.

Structure family	$a_{M_vX}$	$b_{M_vX}$ , kJ/mol	$\beta_{M_vX}$ , kJ/mol nm	$R^2$
Carbonate	0.2780	-3325.75	197.24	0.96
Hydroxide	0.1590	-1474.09	791.70	0.99
Oxide	0.2710	-1984.75	197.24	1.00
Sulfate	0.3470	-842.95	26.32	0.93
Ti perovskite	0.2742	-4620.00	2.80	1.00
Zr perovskite	0.2742	-5129.00	2.80	1.00
Ti pyrochlore	0.0840	-3640.00	82.30	1.00
Zr pyrochlore	0.0830	-3920.00	83.18	1.00

The correlation coefficients are from  $\Delta G_{f,M_vX}^0 - \beta_{M_vX} r_{M^{3+}} = a_{M_vX} \Delta G_{h,M^{3+}}^0 + b_{M_vX}$ . All calculations are at 25°C and 1 bar.

TABLE 2: Thermochemical cycles used to calculate formation enthalpies from elements for  $M_2Ti_2O_7$  ( $\Delta H_{f,M_2Ti_2O_7}^0$ ),  $M_2Zr_2O_7$  ( $\Delta H_{f,M_2Zr_2O_7}^0$ ),  $M_2(ZrO_3)_3$ , ( $\Delta H_{f,M_2(ZrO_3)_3}^0$ ),  $M_2(TiO_3)_3$ , and ( $\Delta H_{f,M_2(TiO_3)_3}^0$ ) solids at 25°C (298.15 K).

$\Delta H_1$	$2RE$ (cr, 298.15 K) + $3/2O_2$ (g, 298.15 K) $\rightarrow$ $RE_2O_3$ (cr, 298.15 K)
$\Delta H_2$	$Ti$ (cr, 298.15 K) + $O_2$ (g, 298.15 K) $\rightarrow$ $TiO_2$ (cr, 298.15 K)
$\Delta H_3$	$Zr$ (cr, 298.15 K) + $O_2$ (g, 298.15 K) $\rightarrow$ $ZrO_2$ (cr, 298.15 K)
$\Delta H_{f,M_2Ti_2O_7}^0$	$= \Delta H_{f,M_2Ti_2O_7-OX} + \Delta H_1 + 2\Delta H_2$ $= [2RE + 2Ti]$ (cr, 298.15 K) + $7/2O_2$ (g, 298.15 K) $\rightarrow$ $RE_2Ti_2O_7$ (cr, 298.15 K)
$\Delta H_{f,M_2Zr_2O_7}^0$	$= \Delta H_{f,M_2Zr_2O_7-OX} + \Delta H_1 + 2\Delta H_3$ $= [2RE + 2Zr]$ (cr, 298.15 K) + $7/2O_2$ (g, 298.15 K) $\rightarrow$ $RE_2Zr_2O_7$ (cr, 298.15 K)
$\Delta H_{f,M_2(ZrO_3)_3}^0$	$= H_{f,M_2(ZrO_3)_3-OX}^0 + \Delta H_1 + 3\Delta H_3$
$\Delta H_{f,M_2(TiO_3)_3}^0$	$= H_{f,M_2(TiO_3)_3-OX}^0 + \Delta H_1 + 3\Delta H_2$

experimental error [27, 28]. Using the previously developed values of  $a_{M_vX}$  for trivalent oxide, hydroxide, carbonate, and sulfate phases of RE and actinides, we related the coefficient  $a_{M_vX}$  to the ratio between the charge of H, C, S, Ti, or Zr and their coordination numbers (CN) or the nearest neighbor in the oxyanions ( $OH^-$  (hydroxide),  $CO_3^{2-}$  (carbonate),  $SO_4^{2-}$  (sulfate),  $TiO_3^{2-}$ ,  $Ti_2O_7^{2-}$  (titanate), and  $Zr_2O_7^{2-}$  (zirconate)) (Figure 1). Based on this relationship we estimated values of  $a_{M_vX}$  for the titanate and zirconate perovskite and pyrochlore families. High ratio of charge/CN indicates strong interaction between the trivalent cation and oxy-anions.

The values of  $a_{M_vX}$  calculated for the zircon and titanate pyrochlores from this relation are 0.083 and 0.084 and that for the perovskite structure is 0.2742 (Table 1). The estimated error of  $a_{M_vX}$  is about 0.001. The error of estimated Gibbs free energy of formation resulting from the error of  $a_{M_vX}$  is within 4 kJ/mol. On the other hand the coefficient  $\beta_{M_vX}$  is related to the structure or the nearest neighbor environment of the cation. The cation with higher CN will have lower value of  $\beta_{M_vX}$  [27]. The  $\beta_{M_vX}$  values for trivalent

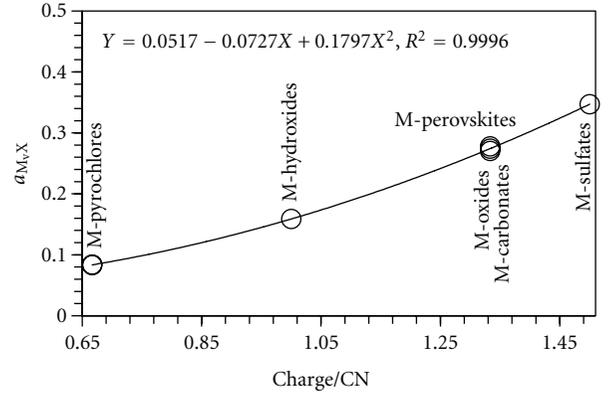


FIGURE 1: A relationship for coefficient  $a_{M_vX}$  and the ratio between charge and coordination number (CN) of the oxyanions oxide, hydroxide, sulfate, carbonate, perovskite and titanate and zirconate pyrochlore structural families. The charge/CN ratios for oxyanions in sulfate, carbonate, oxide, hydroxide, perovskite and titanate and zirconate pyrochlore families are 6/4, 4/3, 4/3, 1/1, 4/3 and 4/6, respectively.

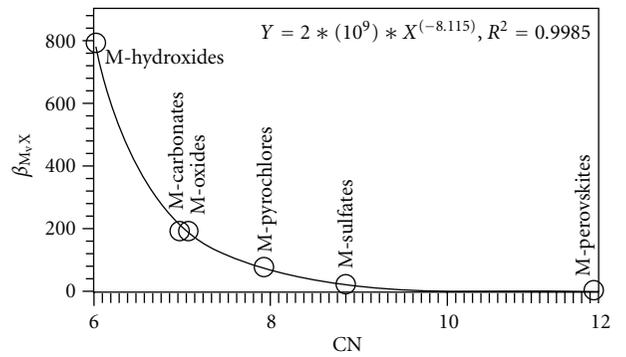


FIGURE 2: A relationship for coefficient  $\beta_{M_vX}$  and the coordination number (CN) of the cations in the sulfate, carbonate, oxide, and hydroxide structural solid phases. The CN for cations in sulfate, carbonate, oxide, hydroxide, perovskite, and pyrochlore families is 9.0, 7.1, 7.0, 6.0, 12.0, and 8.0 respectively.

hydroxide family (CN = 6), carbonate family (CN = 7.1), and sulfate family (CN = 9) are estimated to be equal to 791.70 kJ/mol nm [29], 197.24 kJ/mol nm [30], and 26.32 kJ/mol nm respectively. The  $\beta_{M_vX}$  value for pyrochlore family (CN = 8) should be lower than those for hydroxide and carbonate families and higher than that for calcite family. From the previously estimated  $\beta_{M_vX}$  values for the hydroxide (CN = 6), carbonate (CN = 7.1), sulfate (CN = 9), and oxide (CN = 7) families of trivalent RE and actinides, we correlated the coefficient  $\beta_{M_vX}$  to the CN of the cation in the respective solid phase (Figure 2). The  $\beta_{M_vX}$  value obtained from this relationship for the perovskite family (CN = 12) is 2.8 kJ/mol nm and for the zirconate and titanate pyrochlore families (CN = 8), respectively, 83.18 kJ/mol nm and 82.30 kJ/mol nm. The total error in the calculation of free energies of formation resulting from the estimated coefficient  $\beta_{M_vX}$  is within 4 kJ/mol.

According to Sverjensky and Molling [27], the coefficient  $b_{M_vX}$  reflects characteristics of the reaction type and conditions under which solid formation took place regardless of the valence of the cation or the stoichiometry of the solid. Using the experimentally measured values of standard state (temperature ( $T$ ) = 298.15 K and pressure = 1 atm.) formation enthalpies from oxides reported in the literature for RE titanate pyrochlores [21] and RE zirconate pyrochlores [20], we calculated the Gibbs free energies of formation as

$$\Delta G_{f,M_vX}^0 = \Delta H_{f,M_vX}^0 - T\Delta S_{f,M_vX}^0, \quad (4)$$

where  $\Delta H_{f,M_vX}^0$  is the standard state enthalpy of formation of the  $M_vX$  compound calculated using the thermochemical cycle shown in Table 2. The enthalpies of formation for perovskite structure ( $\Delta H_{ABO_3,OX}$ ) were calculated from constituent oxides by the following equation [31]:

$$\Delta H_{ABO_3,OX} = 2[-60 + 500(1 - t)], \quad \text{kJ/mol}, \quad (5)$$

where  $t$  is the tolerance factor for  $ABO_3$  perovskites [31]. For an ideal perovskite structure (CN of the A site cation = 12)  $t$  is equal to 1.0 [31]. The thermochemical cycles used to calculate the Gibbs free energies of formation from the experimental enthalpies of formation and entropies of formation of the RE and actinide zirconate and titanate pyrochlore and perovskite phases are shown in Table 3.

The entropies of formation ( $\Delta S_{f,M_vX}^0$ ) are calculated and available only for few RE and actinide perovskite and pyrochlore phases. We developed a relationship to estimate the entropy of formation of RE and actinide perovskite and pyrochlore phases from constituent oxides ( $\Delta S_{f,OX}^0$ ) applicable to all trivalent RE and actinide perovskite and pyrochlore families based on the empirical parameter  $\Delta S_{M^{z+}}$ , in J/mol, defined as the difference between the measured entropies of formation of the oxides ( $\Delta S_{f,MO_n}^0(c)$ ) and the measured entropies of formation of the aqueous cation ( $\Delta S_{f,M^{z+}}^0(aq)$ ) of RE and actinides as

$$\Delta S_{M^{z+}} = \frac{1}{x[\Delta S_{f,MO_n}^0(c) - \Delta S_{f,M^{z+}}^0(aq)]}, \quad \text{kJ/mol}, \quad (6)$$

where  $z$  is the charge of the cation ( $z = 3$  for trivalent RE and actinides) and  $x$  is the number of oxygen atoms combined with one atom of M in the oxide ( $x = z/2$ ).  $\Delta S_{M^{z+}}$  in (6) refers to one oxygen atom and characterizes the oxygen affinity of the cation,  $M^{z+}$ . Experimental values of  $\Delta S_{f,MO_n}^0$  of RE and actinides were obtained from [32] and those of  $\Delta S_{f,M^{z+}}^0(aq)$  were obtained from [33]. The entropy of formation from constituent oxides is considered as the sum of the products of the molar fraction of an oxygen atom bound to the two cations ((i) RE or actinide cation and (ii) Zr or Ti cation) in the pyrochlore and perovskite structure. Vieillard [34] showed the dependence of a cation on the oxygen affinity by the difference of electronegativity between cation and oxygen. Previous authors have developed empirical relationship between Gibbs free energy of formation from constituent oxides and the oxygen affinity of cation for

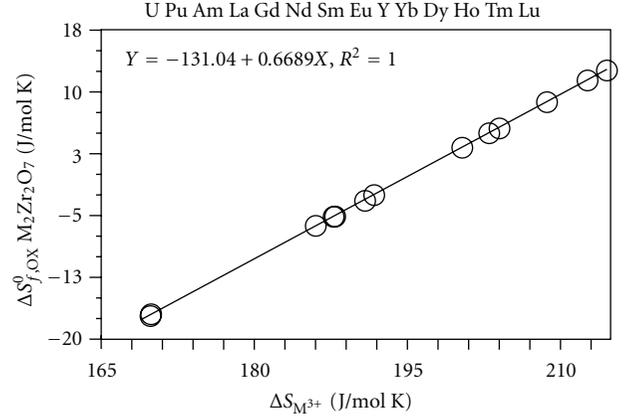


FIGURE 3: A relationship for entropy of formation from oxides ( $\Delta S_{f,OX}^0$ ) in J/mol K and the empirical oxygen affinity parameter ( $\Delta S_{M^{3+}}$ ) in J/mol K shown for the zirconate pyrochlore ( $M_2Zr_2O_7$ ) family. The relationship is estimated as  $\Delta S_{f,OX}^0 = 71.07 - 0.2162\Delta S_{M^{3+}}$ . Standard molar entropies of the oxides and those of aqueous cations are from [32, 33], respectively.

crystalline solids [35–38]. The entropies of formation from constituent oxides ( $\Delta S_{f,OX}^0$ ) were estimated in this article from the empirical parameter ( $\Delta S_{M^{z+}}$ ) by minimizing the difference between experimental entropies [39, 40] and the calculated entropies of formation from constituent oxides as

$$\Delta S_{f,OX}^0 = A' + B'\Delta S_{M^{z+}}. \quad (7)$$

The estimated  $A'$  and  $B'$  coefficients for titanate pyrochlores (Figure 3) are  $-58.47$  and  $-0.2162$  ( $R^2 = 1.0$ ) and for zirconate pyrochlores (Figure 4) are  $71.07$  and  $-0.2162$  ( $R^2 = 1.0$ ). The total error in the free energies of formation using  $\Delta S_{f,OX}^0$  thus estimated is within  $0.5$  kJ/mol.

The estimated Gibbs free energies of formation for the titanate perovskite and the zirconate perovskite are shown in Figures 5 and 6. The calculated (from (4)) standard state Gibbs free energies of formation using the experimentally measured enthalpy and estimated entropy values and the estimated standard Gibbs free energies of formation for the zirconate perovskites ( $M_2(Zr_2O_3)_3$ ) and for the titanate ( $M_2Ti_2O_7$ ) and zirconate ( $M_2Zr_2O_7$ ) pyrochlore families are listed in Table 4.

## 5. Effect of Cations on the Formation of Solids

Using the estimated linear free energies of formation for the perovskite phases and the pyrochlore phases and the formation energies for rutile ( $TiO_2$ ) and zirconia ( $ZrO_2$ ), the effect of cations on the energies of the following pyrochlore formation reactions at room temperature were characterized:



The Gibbs free energies ( $\Delta G_{f,M_vX-OX}^0$ ) across the reactions in (8) are all negative (Table 4). All pyrochlore phases

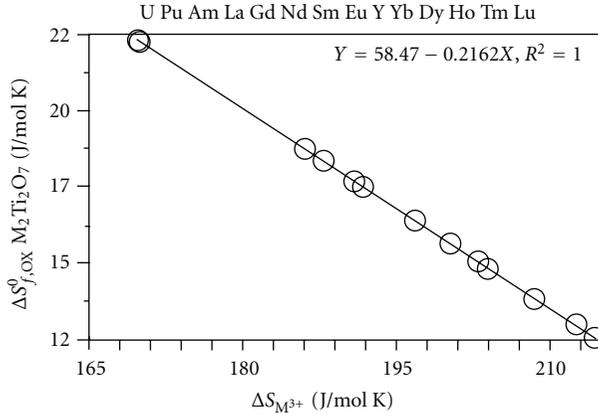


FIGURE 4: A relationship for entropy of formation from oxides ( $\Delta S_{f,OX}^0$ ) in J/mol K and the empirical oxygen affinity parameter ( $\Delta S_{M^{3+}}^0$ ) in J/mol K shown for the titanate pyrochlore ( $M_2Ti_2O_7$ ) family. The relationship is estimated as  $\Delta S_{f,OX}^0 = 58.47 - 0.2162 \Delta S_{M^{3+}}^0$ . Standard molar entropies of the oxides and that of aqueous cations are from [32, 33], respectively.

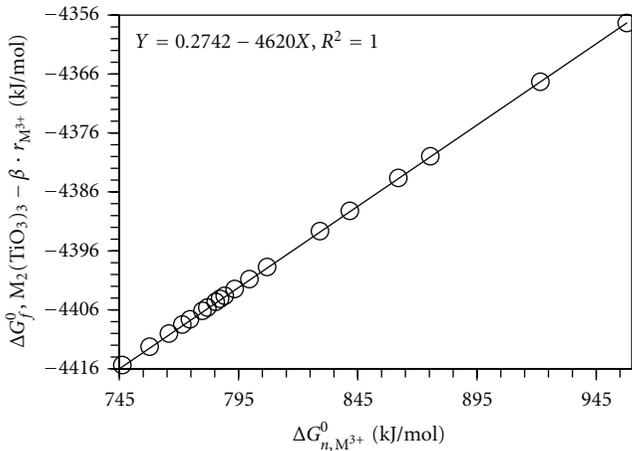


FIGURE 5: Linear free energy relationship of (1) for the isostructural family of  $M_2(TiO_3)_3$  perovskite.

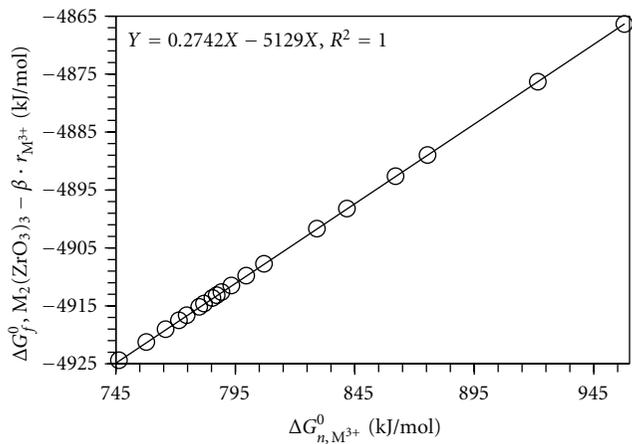


FIGURE 6: Linear free energy relationship of (1) for the isostructural family of  $M_2(ZrO_3)_3$  perovskite.

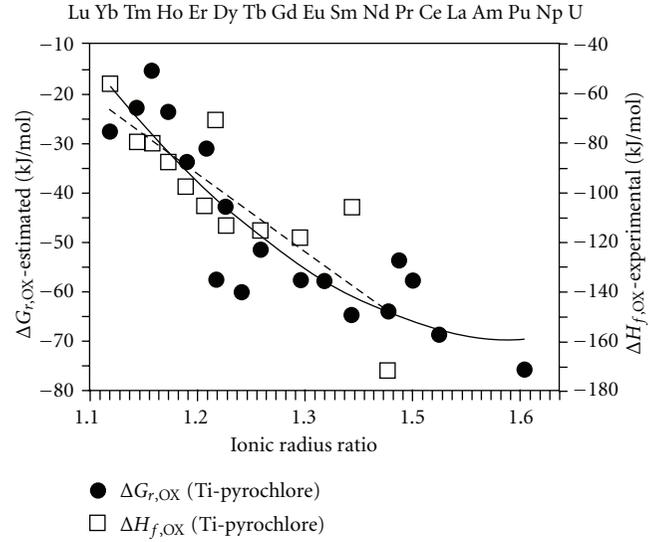


FIGURE 7: A plot of the free energy of reaction for the formation of titanate pyrochlore from constituent oxides ( $\Delta G_{r,OX}$ ) by (8) in kJ/mol shown as a function of the radius ratio of the A site (RE and actinide) cation and the B site (Ti) cation (closed circles) with a nonlinear regression fit (solid line,  $R^2 = 0.80$ ). The experimentally measured formation enthalpies of titanate pyrochlores from constituent oxides ( $\Delta H_{f,OX}$ ) of twelve rare earth cations (from [21]) are also shown as a function of the radius ratio (open squares) with a linear regression fit (dashed line,  $R^2 = 0.71$ ) for comparison.

TABLE 3: Thermochemical cycles used to calculate formation enthalpies ( $\Delta H_f^0$ )<sup>a</sup>, formation entropies ( $\Delta S_f^0$ ), and formation energies ( $\Delta G_f^0$ )<sup>b</sup> from the elements. A complete cycle is shown using  $RE_2Ti_2O_7$  as an example. All calculations are at temperature ( $T$ ) equal to 25°C (298.15 K).

$\Delta H_1$	$2RE$ (cr, 298 K) + $3/2O_2$ (g, 298 K) $\rightarrow$ $RE_2O_3$ (cr, 298 K)
$\Delta H_2$	$Ti$ (cr, 298 K) + $O_2$ (g, 298 K) $\rightarrow$ $TiO_2$ (cr, 298 K)
$\Delta H_f^0$	$= \Delta H_{f-ox} + \Delta H_1 + \Delta H_2$ $= [2RE + 2Ti]$ (cr, 298 K) + $7/2O_2$ (g, 298 K) $\rightarrow$ $RE_2Ti_2O_7$ (cr, 298 K)
$\Delta S_1$	$2RE$ (cr, 298 K) + $3/2O_2$ (g, 298 K) $\rightarrow$ $RE_2O_3$ (cr, 298 K)
$\Delta S_2$	$Ti$ (cr, 298 K) + $O_2$ (g, 298 K) $\rightarrow$ $TiO_2$ (cr, 298 K)
$\Delta S_f^0$	$= \Delta S_{f-ox} + \Delta S_1 + \Delta S_2$ $= [2RE + 2Ti]$ (cr, 298 K) + $7/2O_2$ (g, 298 K) $\rightarrow$ $RE_2Ti_2O_7$ (cr, 298 K)
$\Delta G_f^0$	$= \Delta H_f^0 - T\Delta S_f^0$

<sup>a</sup>Thermodynamic cycles for all solids are shown in Table 2. <sup>b</sup>Data are reported in Table 4.

are expected to be stable with respect to  $M_2O_3$ ,  $M_2(TiO_3)_3$  and  $TiO_2$  even at room temperature. The zircon pyrochlores in (9) are less stable by 50.09 kJ/mol than the titanate pyrochlores at room temperature. These findings are consistent with the findings from previous studies. The reaction energies by (8) and the experimentally measured enthalpies of formation from constituent oxides used to calculate the free energies are shown in Figure 7. The calculated reaction energies show that large cations (e.g., La, Ce, and Pr) form

TABLE 4: Ionic radii and thermodynamic data for aqueous cations and estimated standard Gibbs free energies of formation for perovskite and pyrochlore families of solids.

$M^{3+}$	$r_{M^{3+}}$ (nm)	$\Delta G_n^0$ (kJ/mol)		$\Delta G_{f,M_vX}^0$ (kJ/mol)				$\Delta G_{r,OX}^0$ (kJ/mol)	
		$M_{(aq)}^{3+}$	Perovskite		Pyrochlore				Pyrochlore ( $M_2Ti_2O_7$ ) (Estim.)
			( $M_2(ZrO_3)_3$ ) (Calc.)	( $M_2(ZrO_3)_3$ ) (Estim.)	( $M_2Ti_2O_7$ ) (Calc.)	( $M_2Ti_2O_7$ ) (Estim.)	( $M_2Zr_2O_7$ ) (Calc.)	( $M_2Zr_2O_7$ ) (Estim.)	
La <sup>3+</sup>	0.1061	757.70	-4835.98	-4920.94	-3583.89	-3567.62	-3842.30	-3848.29	-63.77
Sm <sup>3+</sup>	0.0964	781.88	-4857.71	-4914.34	-3530.10	-3566.39	-3829.52	-3847.09	-51.40
Gd <sup>3+</sup>	0.0938	789.21	-4855.00	-4912.34	-3544.03	-3565.99	-3817.44	-3846.69	-42.78
Tb <sup>3+</sup>	0.0923	799.51	—	-4909.52	—	-3565.24	—	-3845.96	-30.89
Dy <sup>3+</sup>	0.0908	787.21	-4894.71	-4912.89	-3570.15	-3566.40	-3850.86	-3847.11	-33.71
Ho <sup>3+</sup>	0.0894	779.85	-4912.01	-4914.91	-3569.08	-3567.13	-3860.59	-3847.84	-23.59
Er <sup>3+</sup>	0.0881	785.41	-4930.46	-4913.39	-3576.73	-3566.78	-3872.94	-3847.48	-15.20
Tm <sup>3+</sup>	0.0870	793.33	-4919.59	-4911.23	-3625.85	-3566.21	-3857.27	-3846.93	-22.84
Yb <sup>3+</sup>	0.0930	806.96	-4945.84	-4907.49	-3500.50	-3565.15	-3790.61	-3845.89	-57.56
Lu <sup>3+</sup>	0.0850	829.12	-4924.03	-4901.42	-3555.91	-3563.36	-3853.82	-3844.11	-27.61
Y <sup>3+</sup>	0.1080	746.28	-4953.24	-4924.07	-3612.56	-3568.42	-3891.27	-3849.08	-35.70
Nd <sup>3+</sup>	0.0995	774.61	-4841.48	-4916.32	-3535.94	-3566.74	-3825.21	-3847.43	-57.67
Ce <sup>3+</sup>	0.1034	771.37	—	-4917.20	—	-3566.70	—	-3847.38	-64.51
Pr <sup>3+</sup>	0.1013	765.77	—	-4918.74	—	-3567.34	—	-3848.01	-57.68
Am <sup>3+</sup>	0.1070	841.66	-4733.58	-4897.92	—	-3560.49	—	-3841.24	-53.65
Np <sup>3+</sup>	0.1100	921.57	—	-4876.00	—	-3553.54	—	-3834.36	-68.75
U <sup>3+</sup>	0.1165	957.85	-4502.28	-4866.03	—	-3549.95	—	-3830.81	-75.70
Pu <sup>3+</sup>	0.1080	862.05	-4758.69	-4892.32	—	-3558.70	—	-3839.47	-57.51
Eu <sup>3+</sup>	0.0950	875.42	-4690.74	-4888.69	-3360.55	-3558.65	-3657.06	-3839.44	-59.79

Cationic radii are from [41]. Values of  $\Delta G_n^0$  of the cations were calculated using  $\Delta G_f^0$  values obtained from [42, 43] as described in [30]. The calculated  $\Delta G_{f,M_vX}^0$  of the perovskite and pyrochlore solid crystals are from (4) by the thermochemical cycles shown in Table 2. The estimated  $\Delta G_{f,M_vX}^0$  values of the perovskite and pyrochlore solid crystals are from (1). Calculated  $\Delta G_{r,OX}^0$  values of the solid titanate pyrochlore solid crystals are from (8) using the estimated  $\Delta G_{f,M_vX}^0$  of the solids. All calculations are at 25°C and 1 bar.

more stable pyrochlores than small cations (e.g., Lu, Tm, and Er) (Figure 7). The relationship between ionic radii of the cations and the formation energies is nonlinear as shown by previous studies [21].

Several mixed oxides in the  $Ln_2ScNbO_7$  series, with Ln = Pr, Eu, Gd, and Dy, were synthesized and found to crystallize in the cubic pyrochlore structure [44]. Ce pyrochlore has been synthesized by sintering oxides of CeO<sub>2</sub>, CaTiO<sub>3</sub>, and TiO<sub>2</sub> [45]. These experimental observations are consistent with our prediction of the negative Gibbs free energy changes across reaction in (8). Although the reaction energy calculation is based on room temperature, the prediction is basically consistent with experimental observation at higher temperatures.

## 6. Conclusions

The linear free energy relationship of Sverjensky and Molling was used to calculate the Gibbs free energies of formation of pyrochlore mineral phases ( $M_2Ti_2O_7$  and  $M_2Zr_2O_7$ ) from known thermodynamic properties of the corresponding aqueous trivalent cations ( $M^{3+}$ ) of several lanthanides and actinides. The coefficients for the structural family of pyrochlore with the stoichiometry of  $M_2Ti_2O_7$

are estimated to be  $a_{M_vX} = 0.084$ ,  $b_{M_vX} = -3640$  kJ/mol, and  $\beta_{M_vX} = 82.30$  kJ/mol nm and those for the  $M_2Zr_2O_7$  are estimated to be  $a_{M_vX} = 0.083$ ,  $b_{M_vX} = -3920$  kJ/mol, and  $\beta_{M_vX} = 83.18$  kJ/mol nm. Thermodynamic properties of fictive mineral phases can also be predicted from this method. These fictive phases cannot be synthesized in the laboratory or occur in the nature, but their thermodynamic properties are required for the immobilization reaction construction of solid solution models for actual crystalline phases. The estimation method is superior because the estimated Gibbs free energies of formation of zirconate and titanate pyrochlore phases are validated with experimentally measured enthalpy and entropy data.

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