



Formation enthalpies and heat capacities of rear earth titanates: RE_2TiO_5 ($RE=La, Nd$ and Gd)

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ABSTRACT

The formation enthalpies and heat capacities of orthorhombic rare earth titanates, RE_2TiO_5 ($RE=La, Nd$ and Gd), have been studied by high temperature differential scanning calorimetry (300–1473 K) and oxide-melt solution calorimetry. The RE_2TiO_5 samples are stable in enthalpy with respect to their oxides and the pyrochlore $RE_2Ti_2O_7$ phase. The general trend that has been demonstrated in other RE -ternary systems; decreasing thermodynamic stability with decreasing R_A/R_B was found to be valid for the RE_2TiO_5 , and their enthalpies of formation from oxides become more negative with increasing RE^{3+} ionic radius.

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1. Introduction

Rare earth titanates have interesting structural and physical properties which promote broad applications in engineering [1–5]. For example, the pyrochlore phase shows potential for use as solid electrolytes, mixed ionic/electronic conducting electrodes [6–9], catalysts [10], ferroelectric/dielectric device components [11], and is a promising material for use as a nuclear waste form ceramic [12–16]. In these compounds, the Ti^{4+} is in six-fold coordination with oxygen, forming a corner-sharing octahedral framework, and the larger lanthanide elements occupy the voids in the framework. However, $La_2Ti_2O_7$ does not have the pyrochlore structure, forming a perovskite-related phase, and the $La-Ti-O$ ternary system shows many homologous polymorphs with different compositions [17]. Additional rare earth titanates with orthorhombic structure and RE_2TiO_5 composition have been reported [18]. In this system, the Ti^{4+} is five-coordinated with oxygen forming an off-center square pyramid, and the neighboring polyhedra are corner-shared, forming a chain along the c -axis (Fig. 1). The coordination number of larger lanthanide elements, RE^{3+} , is 7 and is lower than in any of the other ternary compounds in the $RE-Ti-O$ ternary systems. Even though this kind of geometry is rare in nature, all light lanthanide titanates from La to Dy (including Y) with RE_2TiO_5 composition maintain it

up to 1573 K. At higher temperatures, the medium-sized lanthanides, $RE=Gd, Tb, Dy, Ho,$ and Y , exhibit hexagonal structures [19,20]. Although the phase relations, pressure-induced structural transformations, and magnetic and electrical properties of the lanthanide titanates have been widely studied [19–22], available thermodynamic data are still incomplete. In this study, the heat capacity (C_p), the heat content between room temperature (298 K) and 975 K, and the formation enthalpy of RE_2TiO_5 (where $RE=La, Nd$ and Gd) were measured and are reported.

2. Experimental

2.1. Sample synthesis and characterization

The rare earth titanates were synthesized by solid state reaction from a mixture of RE_2O_3 (Alfa Aesar, mass fraction purity 0.9999) and TiO_2 (Alfa Aesar, mass fraction purity 0.9995) powders. The precursor materials were dried overnight at 1273 K. The required amounts were weighed and ground together in an agate mortar. The powders were then manually pressed into pellets with a diameter of 7 mm, and fired at 1573 K in air for 96 h. The pellets were then reground, re-compacted, and fired for 36 h at 1573 K twice. The heating and cooling rates were 10 K min^{-1} for each step. The resulting ceramics were analyzed by powder X-ray diffraction (XRD) and electron probe micro-analysis (EPMA). The XRD was performed using a Bruker D8 Advance diffractometer (Bruker, Madison, WI) with $CuK\alpha_1$ radiation and a rotating sample holder. The operating parameters were 40 kV and 40 mA, with a 2θ step size of 0.01° and 3 s/step. LaB6 (NIST 660a) [23] was used as a standard for the cell parameter determination. The structure refinements were carried out by the Rietveld method

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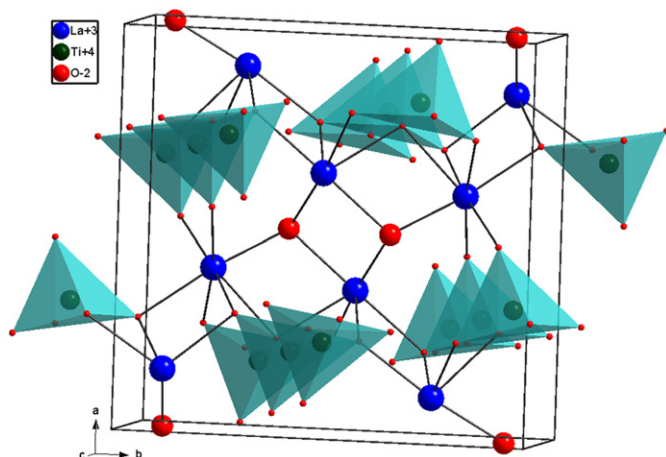


Fig. 1. Schematic crystal structure of orthorhombic La_2TiO_5 with space group $Pn\bar{a}m$ (ICSD #28277).

using the FullProf program in the Winplotr platform [24]. In the current work the atomic displacement parameters were fixed. A Cameca SX-100 electron microprobe (Cameca, ID) was used for chemical analysis. Energy dispersive spectroscopy, backscattered electron imaging (BSE) and characteristic x-ray dot mapping were used for characterization of sample homogeneity. Wavelength dispersive spectroscopy (WDS) was used for quantitative chemical analysis.

2.2. Calorimetry

2.2.1. Heat capacity measurements

The heat capacity, C_p , of RE_2TiO_5 was measured between 300 and 1473 K utilizing a Netzsch high temperature differential scanning calorimeter, DSC 404 (Netzsch, Selb, Germany) [25], operated in continuous mode. Temperature calibration was done in the heating direction using the melting of Sn, Ag and Au standards in alumina crucibles. Single crystal Al_2O_3 was used as a sensitivity calibrant. The $C_{p,m}$ equation of $\alpha\text{-Al}_2\text{O}_3$ provided by NIST was used for the standard [26]. The errors in heat capacity were estimated by running ZrO_2 (99.978%, Alfa-Aesar) powder and comparing with tabulated data [27]. The estimated accuracy in heat capacity is 2–5% with the highest error at high temperature. The measurements were carried out by continuous heating at 10 K/min and using 10 min isothermal holds at 300 and 1473 K in the heating direction. The RE_2TiO_5 powders were ground lightly, and then put into a sample crucible tightly to ensure good thermal contact. About 50 mg of RE_2TiO_5 was used for each measurement. On the reference side, an empty reference crucible was in place.

2.2.2. Transposed temperature drop calorimetry (TTD)

Transposed temperature drop calorimetry (TTD) was used a custom-built Tian–Calvet twin calorimeter at 975 K. Details of the equipment, calibration and experimental procedure are described elsewhere [28,29]. These references also discuss appropriate calibration procedures. In the TTD experiment, a pelletized powdered sample (~ 5 mg) is dropped into a hot calorimeter in the absence of solvent. The heat effect measured is equal to the heat content of the sample, $\Delta H = \int_{298}^T C_p dT$, if no phase transformation or decomposition occurs.

2.2.3. High-temperature oxide melt solution calorimetry

High-temperature oxide melt solution calorimetry was performed in a custom-built Tian–Calvet twin calorimeter at 1083 K. Details of the equipment calibration and experimental

procedure are described elsewhere [28,29]. Pelletized samples (~ 10 mg) were dropped into a platinum crucible containing 20 g of sodium molybdate ($3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$) solvent. Oxygen gas was flushed through the calorimeter assembly and bubbled through the solvent in order to enhance the dissolution. The drop solution enthalpy value for the end member oxides (TiO_2 , La_2O_3 , Nd_2O_3 and Gd_2O_3) are a necessary component of the thermochemical cycle. Since more than one polymorphic form is possible, the sesquioxides of Nd and Gd and the TiO_2 were dried at 1373 K for 12 h and stabilized in the hexagonal (A, $P3m1$), cubic (C, $Ia3$, bixbyite type) and the rutile forms, respectively. Since La_2O_3 is highly hygroscopic, the materials were dried and stabilized inside an argon-filled glove box at 1373 K for 12 h in the hexagonal (A, $P3m1$) form. Then, the La_2O_3 samples were weighted in the glovebox and dropped into the calorimeter from sealed vials to minimize exposure to the environment.

3. Results and discussion

The measured XRD patterns confirmed that the synthesized La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 are orthorhombic, and they refined well with space group $Pn\bar{a}m$ (Fig. 2). No additional phases were indicated by the XRD measurements. The lattice parameters, atomic coordinates and fitting results are listed in Table 1. The structural parameters of La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 are in good agreement with those of La_2TiO_5 and Nd_2TiO_5 [22] and Gd_2TiO_5 [19].

The chemical compositions of the samples were measured by EPMA and the results are listed in Table 2. For each sample, between 11 and 16 points were analyzed, and the compositions

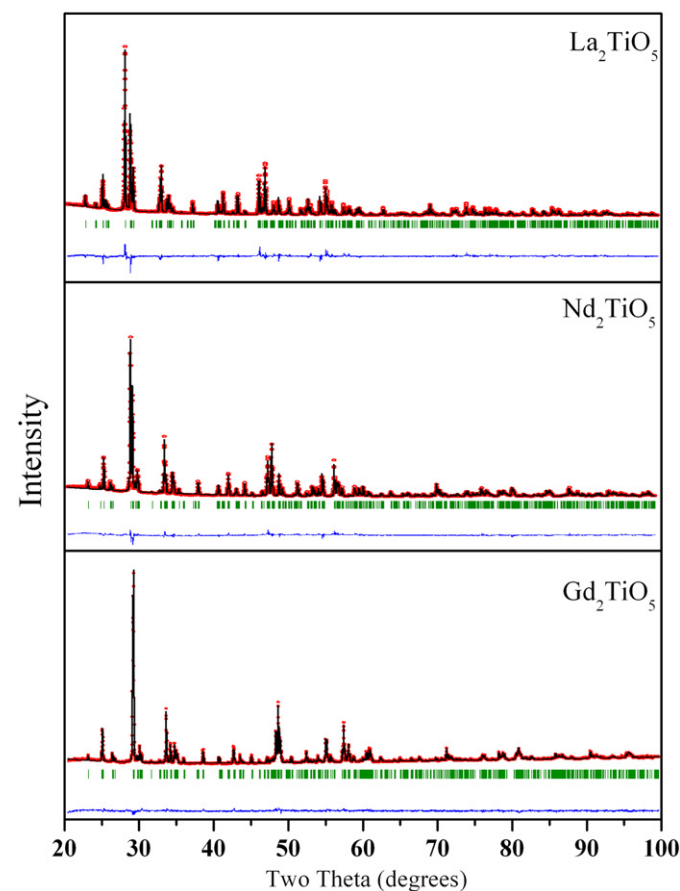


Fig. 2. X-ray diffraction pattern and Rietveld refinement results of the XRD patterns of La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 samples.

Table 1
Refined atomic coordinates and lattice parameters of orthorhombic La₂TiO₅, Nd₂TiO₅ and Gd₂TiO₅ with *Pnma* space group.

RE		La	Nd	Gd	La	Nd	Gd	La	Nd	Gd
Cell parameter (Å)		<i>A</i>			<i>b</i>			<i>c</i>		
		11.0044(1)	10.7252(3)	10.476(2)	11.3922(1)	11.3620(3)	11.319(2)	3.9446(3)	3.8428(1)	3.756(6)
Atom	<i>W</i> _{Yckoff}	<i>X</i>			<i>y</i>			<i>z</i>		
<i>RE</i> ₁	4c	0.13585(13)	0.13587(14)	0.13693(17)	0.06141(11)	0.05994(12)	0.05749(14)	0.25	0.25	0.25
<i>RE</i> ₂	4c	0.40464(12)	0.39703(13)	0.38943(16)	0.21426(11)	0.21919(12)	0.22175(14)	0.75	0.75	0.75
Ti ₁	4c	0.19363(31)	0.18561(28)	0.17856(39)	0.37143(33)	0.3715(42)	0.37698(50)	0.25	0.25	0.25
O ₁	4c	0.00770(107)	0.00469(98)	0.23152(147)	0.10376(112)	0.10443(120)	0.54443(151)	0.75	0.75	0.75
O ₂	4c	0.27700(105)	0.28331(95)	0.48802(149)	0.03160(113)	0.02466(121)	0.61202(151)	0.75	0.75	0.75
O ₃	4c	0.23257(94)	0.23098(120)	0.27422(130)	0.37455(108)	0.37695(105)	0.88461(166)	0.75	0.75	0.75
O ₄	4c	0.28299(105)	0.25803(110)	0.00379(127)	0.23678(95)	0.23078(100)	0.34762(126)	0.25	0.25	0.25
O ₅	4c	0.04529(109)	0.02628(120)	0.26261(161)	0.32236(108)	0.33781(95)	0.23038(153)	0.25	0.25	0.25
Fitting results		<i>R</i> _b (%)	<i>R</i> _p (%)	<i>R</i> _{wp} (%)	χ^2					
La ₂ TiO ₅		5.49	10.4	11.0	1.41					
Nd ₂ TiO ₅		6.38	11.2	10.1	2.69					
Gd ₂ TiO ₅		7.68	17.3	10.7	1.62					

Table 2
EMPA-WDS analyses of the RE₂TiO₅. The standards used were TiO₂, and REPO₄.

RE	TiO ₂ (wt%)	RE ₂ O ₃ (wt%)	Total (wt%)	<i>N</i>	Formula
La	18.64 ± 0.13	79.43 ± 0.40	98.07 ± 0.48	11	La _{2.05 ± 0.07} Ti _{0.96 ± 0.06} O _{4.99 ± 0.01}
Nd	18.89 ± 0.11	80.34 ± 0.30	99.24 ± 0.34	16	Nd _{2.01 ± 0.05} Ti _{0.99 ± 0.04} O _{4.99 ± 0.01}
Gd	18.02 ± 0.17	81.34 ± 0.67	99.36 ± 0.79	13	Gd _{1.99 ± 0.04} Ti _{1.00 ± 0.05} O _{5.00 ± 0.02}

presented are the average value with error given as two standard deviation of the mean. The resulting average compositions are La_{2.05 ± 0.07}Ti_{0.96 ± 0.06}O_{4.99 ± 0.01}, Nd_{2.01 ± 0.05}Ti_{0.99 ± 0.04}O_{4.99 ± 0.01} and Gd_{1.99 ± 0.04}Ti_{1.00 ± 0.05}O_{5.00 ± 0.02}. In addition, EDS analysis does not reveal any significant contamination of the samples. We employ the nominal composition in the thermodynamic calculation below.

Representative curves of the heat capacity, *C_p*, of RE₂TiO₅ (*RE*=La, Nd, and Gd) are presented in Fig. 3. Values from the Neumann–Kopp relation based on the data from [30] are also shown for comparison. A three-parameter polynomial equation for the heat capacity

$$C_p(T) = a + bT(K) + C(T(K))^{-1} \quad (1)$$

and the corresponding integrated form for the enthalpy

$$H(T) - H(T)_{298\text{K}} = aT(K) + \frac{b}{2}(T(K))^2 + C\ln(T(K)) \quad (2)$$

were applied.

From the fitting procedure, we obtain a set of $\Delta H_{298\text{K}}^T$ and *C_p* equations for each phase as follows:

La₂TiO₅ (from 298 to 1400 K):

$$C_p(\text{J mol}^{-1}) = 202.50 + 0.0239(T/K) - 21261.97(T/K)^{-1} \quad (3)$$

$$H(T) - H(T)_{298\text{K}}(\text{J mol}^{-1}) = 202.50(T/K) + 0.0112(T/K)^2 + 21262.97\ln(T/K) \quad (4)$$

Nd₂TiO₅ (from 298 to 1400 K):

$$C_p(\text{J mol}^{-1}) = 256.66 + 0.0044(T/K) - 29655.07(T/K)^{-1} \quad (5)$$

$$H(T) - H(T)_{298\text{K}}(\text{J mol}^{-1}) = 256.66(T/K) + 0.0022(T/K)^2 + 29655.07\ln(T/K) \quad (6)$$

Gd₂TiO₅ (from 298 to 1400 K):

$$C_p(\text{J mol}^{-1}) = 234.45 + 0.0008(T/K) - 22780.24(T/K)^{-1} \quad (7)$$

$$H(T) - H(T)_{298\text{K}}(\text{J mol}^{-1}) = 234.45(T/K) + 0.0004(T/K)^2 + 22,780.24\ln(T/K) \quad (8)$$

The heat content between room temperature (298 K) and 975 K for each RE₂TiO₅ titanate was measured by transposed temperature drop calorimetry (TTD) using the custom-built Tian–Calvet twin calorimeter at 975 K. The measured enthalpies 121.24 ± 4.46, 134.34 ± 1.02 and 131.22 ± 3.25 kJ/mol are in very good agreements with the calculated enthalpy from the measured heat capacity 122.39 ± 2.75, 136.92 ± 1.75 and 132.28 ± 1.74 kJ/mol for the La-, Nd- and Gd-titanate samples, respectively. The deviation in heat capacity values from that calculated using the Neumann–Kopp rule are about 4.5 ± 3.7, 1.5 ± 0.8 and 4.3 ± 0.47% for La-, Nd- and Gd-titanate samples, respectively, with the highest error at low temperature. Moreover, the data of Panneerselvam et al. [31] for Gd₂TiO₅ are given in Fig. 3. There is reasonable agreement between this two set of measurements, the average deviation in heat capacity values from Ref. [31] and our measurement is 4.3 ± 1.7%. Thus, using the Neumann–Kopp rule, one can make a good approximation to the heat capacity for the rare earth titanate using the constituent oxide values. At temperatures near and below ambient, this approximation breaks down. Cryogenic calorimetry for near 0 K to ambient would need to be done to obtain low temperature heat capacities and standard entropies of these materials.

The average enthalpies of drop solution for the TiO₂, RE₂O₃, and the titanate samples, and two standard deviations of the mean were calculated from the seven to twelve measurements for each sample and are summarized in Table 3. The formation enthalpies from oxides, using the drop solution enthalpies, were

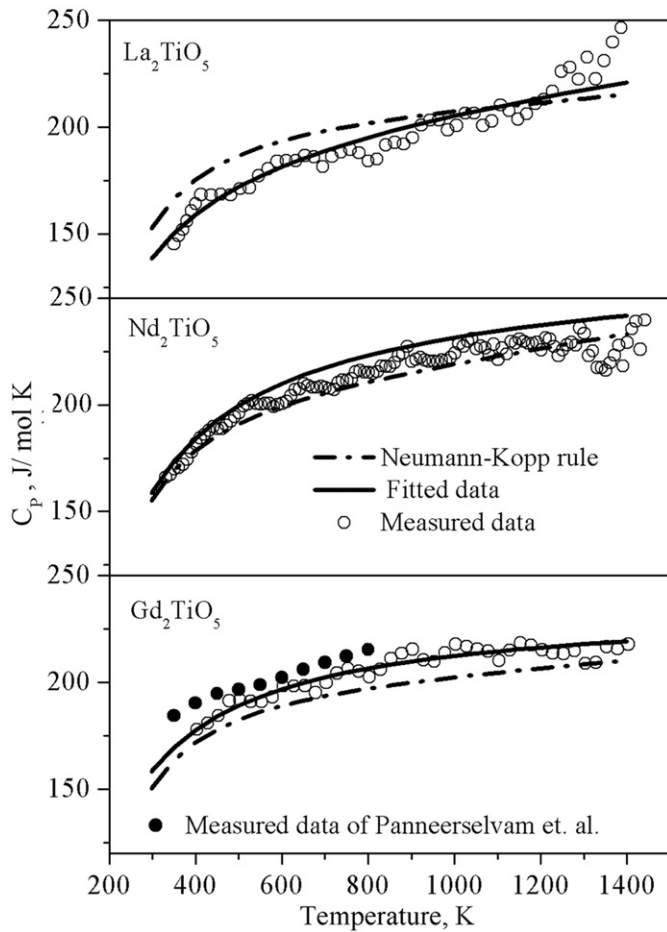


Fig. 3. Isobaric molar heat capacity, C_p , of La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 samples. The fitted and calculated using Neumann-Kopp rule heat capacities are also presented.

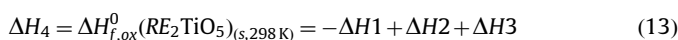
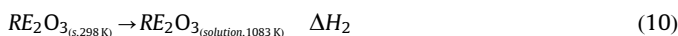
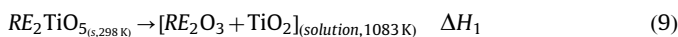
Table 3
Enthalpies of drop solution (ΔH_{ds}) in $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ at 1083 K and enthalpies of formation from oxide ($\Delta H_{f,ox}^0$) at 298 K.

Cation	ΔH_{ds} titanate	ΔH_{ds} oxides, RE_2O_3	$\Delta H_{f,ox}^0$, RE_2TiO_5	$\Delta H_{f,ox}^0$, $\text{RE}_2\text{Ti}_2\text{O}_7$ [32]
La	-23.02 ± 2.32	-209.71 ± 5.35	-112.99 ± 4.46	-205.68 ± 2.8^a
Nd	15.18 ± 0.53	-142.2 ± 1.17	-84.03 ± 0.45	-147.38^b
Gd	24.62 ± 1.19	-121.00 ± 3.20	-72.75 ± 1.15	-113.4 ± 2.7
Ti	–	73.70 ± 0.39		

^a The $\Delta H_{f,ox}^0(\text{La}_2\text{Ti}_2\text{O}_7)$ was corrected according to the appendix in [33].

^b The value for the $\text{Nd}_2\text{Ti}_2\text{O}_7$ pyrochlore formation enthalpy was estimated using the simple linear relationship $\Delta H_{f,ox}^0(\text{Pyrochlore}) = -378.12(R_A/R_B) + 545.74$ in [32].

determined using the following thermodynamic cycle:



where ΔH_1 , ΔH_2 , and ΔH_3 are drop solution enthalpies for La, Nd and Gd oxide, titanium oxide and the rare earth titanates,

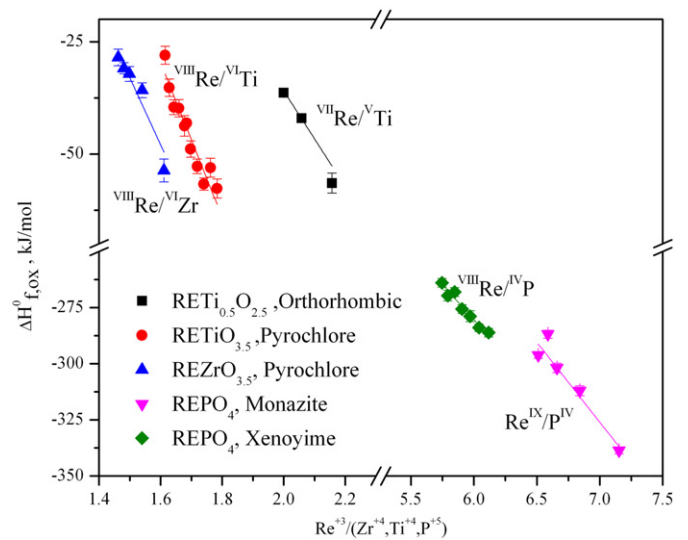
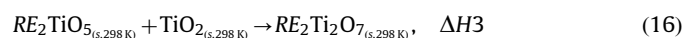
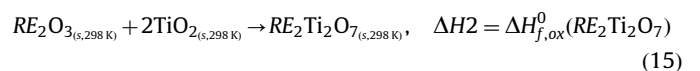
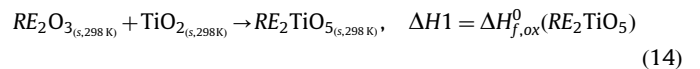


Fig. 4. Normalized enthalpy of formation for one RE^{3+} cation from the oxides for several RE ternary oxide systems vs. the cation radius ratio R_A/R_B ($A=\text{RE}$, $B=\text{Ti}$, Zr , P) [32,34]. All the RE ternary oxide systems are stable relative to constituent oxides, with increasing stability as R_A/R_B increases. The Roman numerals above the cations represent the coordination number.

respectively. The enthalpies of formation $\Delta H_{f,ox}^0$ calculated from the above thermodynamic cycle are summarized in Table 3.

The measured formation enthalpies show that the rare earth titanates, RE_2TiO_5 , are energetically stable with respect to their constituent oxides. Moreover, the general trend that has been demonstrated for other rare earth ternary compounds [32] is also valid for the orthorhombic RE-titanates (RE_2TiO_5), where the thermodynamic stability decreases as R_A/R_B ($A=\text{RE}$, $B=\text{Ti}$) decreases (Fig. 4).

The stability relation between RE_2TiO_5 and $\text{RE}_2\text{Ti}_2\text{O}_7$ can be assessed using the heats of formation from this work and published data [32] (Table 3). The formation enthalpy of $\text{RE}_2\text{Ti}_2\text{O}_7$ pyrochlore from the reaction between RE_2TiO_5 and TiO_2 can be calculated according to



$$\Delta H3 = -\Delta H1 + \Delta H2 \quad (17)$$

This reaction was found to be exothermic (La -94 kJ/mol, Nd -63 kJ/mol and Gd -40 kJ/mol), and becomes increasingly exothermic as the rare earth ionic radius (RE^{3+}) decreases. However, the reaction $2\text{RE}_2\text{TiO}_5 = \text{RE}_2\text{Ti}_2\text{O}_7 + \text{RE}_2\text{O}_3$ is endothermic (La 20 kJ/mol, Nd 21 kJ/mol and Gd 32 kJ/mol), with an opposite dependence on the rare earth ionic radius. Therefore, each phase, RE_2TiO_5 or $\text{RE}_2\text{Ti}_2\text{O}_7$, is energetically stable at its own composition. Given these large energetic effects and that entropies of solid state reactions are generally small; we conclude that these phases are stable in Gibbs free energy as well.

4. Summary

The thermodynamic properties of the orthorhombic phases La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 were studied using differential

scanning calorimetry, transposed temperature drop calorimetry, and high temperature oxide-melt solution calorimetry. The RE_2TiO_5 samples were stable in enthalpy with respect to their oxides and the pyrochlore $RE_2Ti_2O_7$ phase. The general trend that has been demonstrated in other RE -ternary systems, decreasing thermodynamic stability with decreasing R_A/R_B was found to be valid for the orthorhombic RE_2TiO_5 also.

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