Enthalpies of formation of rare earth orthovanadates, $REVO_4$

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Abstract

Rare earth orthovanadates, $REVO_4$, having the zircon structure, form a series of materials interesting for magnetic, optical, sensor, and electronic applications. Enthalpies of formation of $REVO_4$ compounds ($RE = $ Sc, Y, Ce–Nd, Sm–Tm, Lu) were determined by oxide melt solution calorimetry in lead borate ($2PbO \cdot 2B_2O_3$) solvent at 1075 K. The enthalpies of formation from oxide components become more negative with increasing RE ionic radius. This trend is similar to that obtained for the rare earth phosphates.
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1. Introduction

Rare earth orthovanadates ($REVO_4$) have been widely studied over the past several years because of their interesting magnetic (e.g., magnetic phase transitions), optical (rare earth-activated luminescence) and electronic (Jahn–Teller phase transitions) properties. They also have practical applications as laser hosts [1], thermophosphors for remote temperature measurements [2], X-ray and γ-ray scintillators for medical imaging applications [3], and chemically durable materials for waste disposal [4,5].

Rare earth orthovanadates crystallize in the tetragonal zircon structure with space group $I4_1/amd$ (141). All the RE ions occupy a site with D_{2d} point group symmetry. Recently, systematic crystallographic and magnetic studies of these compounds have been made using inelastic neutron scattering and magnetic susceptibility measurements [6–8]. However, thermodynamic data for these compounds are both incomplete and somewhat contradictory. The heats of formation of some $REVO_4$ compounds ($RE = $ Y, La, Sm, Nd and Gd) and the apparent activation energies of their synthesis were reported by Zielinski and Skupin [9] from thermal analysis. Phase diagrams for RE_2O_3–V_2O_5 systems ($RE = $ Gd–Lu) were constructed by Rykova et al. [10–16]. In addition, standard enthalpies of formation and heat capacities of the $REVO_4$ compounds were estimated from exothermic DTA peaks near 943 K [17–19]. Kitayama et al. [20] measured the equilibrium oxygen partial pressures at 1473 K in the rare earth—vanadium—oxygen systems, and Yokokawa et al. [21] evaluated the thermodynamic properties of $REVO_4$ compounds using Kitayama's results. There are, however, discrepancies of 10–50 kJ/mol in the published enthalpies of formation from the elements [9–17] (see Table 1). In order to resolve these differences we have determined the enthalpies of formation of the rare earth orthovanadates directly by high-temperature oxide melt solution calorimetry. This method provides enthalpies of formation directly by comparing the heats of solution of the compound and its constituent oxides [22–24].

2. Experimental methods and sample characterization

The sesquioxides RE_2O_3 ($RE = $ Sc, Nd, Eu, Ho and Tm) as well as cerium oxide, CeO_2, and vanadium pentoxide, V_2O_5, were purchased from Alfa Aesar with purity > 99.9 wt% on a metals basis. Synthesis and calorimetry of Tb_2O_3 have been discussed by Ushakov et al. [25] and the terbium remains trivalent upon dissolution in the melt.

The vanadates were initially prepared in single crystal form by a high-temperature solution (flux) growth process

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[4]. In a standard flux growth run, 73.33 g of PbO, 30.67 g of V_2O_5 and 3.3 g of the RE_2O_3 were placed in a Pt crucible and heated to 1633 K. After soaking for 10–12 h at 1633 K, the temperature was lowered at a linear rate of 1.0 K/h to 1173 K. At this point, the crucible was removed from the furnace, and the flux was decanted. Final removal of the residual solidified $Pb_2V_2O_7$ growth flux was accomplished by cleaning in nitric acid. The as-grown vanadate single crystals exhibited a bar-like prismatic habit with the long axis of the bar lying along the tetragonal c axis of the material.

The crystals were ground into powder for calorimetry. X-ray diffraction (XRD) analyses were carried out with a Scintag PAD V diffractometer with Cu $K\alpha$ radiation. Data

were collected in the $2-\theta$ range of 15–100° with a step size of 0.02° and a dwell time of 2 s.

High-temperature oxide-melt solution calorimetry was carried out at 1075 K with a custom built Tian–Calvet calorimeter described elsewhere [22–24]. Lead borate ($2Pb \cdot B_2O_3$) was used as a solvent. The headspace above the solvent was flushed with oxygen gas at a rate of 35 mL/min. The samples were pressed into pellets and weighed in air. Terbium oxide required special handling because of its possible tendency to oxidize. It was pelletized in a glove box filled with Ar and transported to the calorimeter in glass vials. The vials with Tb_2O_3 pellets were opened directly before dropping the samples into the calorimeter so that the air-exposure time was less than 3 s. Approximately 5 and 15-mg pellets were used per experiment and no more than 50–60 mg of the sample was dissolved per 30 g of solvent.

The calorimetric measurements were calibrated against the heat content of 5 mg alumina pellets dropped from room temperature into the calorimeter. This is a standard procedure [24]. Six to 11 data points were collected for each compound except for ScVO$_4$. In this case, only three pellets were dropped because of the small amount of sample available.

3. Results

X-ray diffraction of the ground powders confirmed that the single crystal material, prepared a number of years ago, has remained single phase. The measured enthalpies of drop solution (ΔH_{ds}) for vanadates, rare earth oxides and vanadium oxide at 1075 K in lead borate solvent and the calculated enthalpies of formation of the vanadates from component oxides at 298 K are listed in Table 2. The

Table 1
Reported enthalpies of formation from elements ($\Delta H_{f, el}$) for rare-earth vanadates at 298 K

	$\Delta H_{f, el}$ (kJ/mol [18])	$\Delta H_{f, el}$ (kJ/mol [17])	$\Delta H_{f, el}$ (kJ/mol [9])	$\Delta H_{f, el}$ (kJ/mol [21])
LuVO$_4$	−1794	−1800	—	−1807
TmVO$_4$	−1804	−1779	—	−1819
ErVO$_4$	−1817	−1809	—	−1828
HoVO$_4$	−1804	−1800	—	−1823
YVO$_4$	−1817	—	−1796	−1839
DyVO$_4$	−1798	−1804	−1793	−1818
TbVO$_4$	−1800	−1796	—	−1826
GdVO$_4$	−1783	−1788	−1783	−1811
EuVO$_4$	−1703	—	—	−1729
SmVO$_4$	−1786	—	−1765	−1815
NdVO$_4$	−1782	—	−1766	−1815
PrVO$_4$	−1785	—	—	−1821
CeVO$_4$	−1781	—	—	−1820

Table 2
Enthalpies of drop solution (ΔH_{ds}) for rare-earth oxides, vanadium pentoxide and rare-earth vanadates at 1075 K in a $2PbO \cdot B_2O_3$ melt, and enthalpies of formation from oxides ($\Delta H_{f, ox}$) and from elements ($\Delta H_{f, el}$) for rare-earth vanadates at 298 K

Rare-earth oxide	ΔH_{ds} (kJ/mol)[c]	Rare-earth vanadates	ΔH_{ds} (kJ/mol)	$\Delta H_{f,el}$ (kJ/mol)	$\Delta H_{f,ox}$ (kJ/mol)
Sc$_2$O$_3$	77.83 ± 1.98 (9)[b]	ScVO$_4$	69.27 ± 1.53 (3)	−1752.2 ± 2.2	−22.4 ± 1.8
Lu$_2$O$_3$	2.54 ± 0.37 (7)[b]	LuVO$_4$	94.80 ± 2.02 (8)	−1799.9 ± 2.3	−85.6 ± 2.0
Tm$_2$O$_3$	18.30 ± 0.82 (8)[b]	TmVO$_4$	108.17 ± 1.94 (6)	−1810.9 ± 2.3	−91.1 ± 1.9
Er$_2$O$_3$	50.06 ± 0.40[a]	ErVO$_4$	106.43 ± 2.93 (8)	−1797.5 ± 3.2	−73.2 ± 2.9
Ho$_2$O$_3$	−23.97 ± 0.32 (7)[b]	HoVO$_4$	104.75 ± 1.50 (10)	−1824.6 ± 1.9	−108.8 ± 1.5
Y$_2$O$_3$	32.80 ± 0.80[a]	YVO$_4$	121.89 ± 1.45 (8)	−1839.2 ± 1.9	−97.5 ± 1.5
Dy$_2$O$_3$	46.90 ± 0.40[a]	DyVO$_4$	105.45 ± 1.70 (8)	−1780.8 ± 2.1	−74.0 ± 1.7
Tb$_2$O$_3$	9.60 ± 0.20 (7)[b]	TbVO$_4$	116.91 ± 1.79 (11)	−1811.9 ± 2.1	−104.2 ± 1.8
Gd$_2$O$_3$	25.70 ± 0.20[a]	GdVO$_4$	129.47 ± 1.02 (6)	−1797.5 ± 1.6	−108.7 ± 1.1
Eu$_2$O$_3$	42.39 ± 0.44 (6)[b]	EuVO$_4$	134.59 ± 1.83 (8)	−1712.2 ± 2.2	−105.4 ± 1.9
Sm$_2$O$_3$	27.30 ± 0.60 (8)[b]	SmVO$_4$	136.51 ± 1.95 (10)	−1802.2 ± 2.3	−114.9 ± 1.9
Nd$_2$O$_3$	14.30 ± 0.90[a]	NdVO$_4$	142.58 ± 1.96 (9)	−1806.8 ± 2.3	−127.5 ± 2.0
Pr$_2$O$_3$	16.50 ± 0.20[a]	PrVO$_4$	139.47 ± 1.33 (7)	−1803.6 ± 1.8	−123.3 ± 1.4
CeO$_2$	83.34 ± 1.86 (7)[b]	CeVO$_4$	97.69 ± 1.88 (8)	−1875.0 ± 3.0	−202.4 ± 5.2
V$_2$O$_5$	−15.92 ± 0.45 (8)[b]				

[a] From [29].
[b] Current work.
[c] The errors are two standard deviations of the mean; numbers in parentheses are the number of experiments performed.

Table 3
Thermochemical cycle for calculation of enthalpy of formation for YVO_4 (representative of other $REVO_4$) and $CeVO_4$

Reaction		ΔH (kJ/mol)
$YVO_4(s,298) \rightarrow 1/2 Y_2O_3(sln,1075) + 1/2 V_2O_5(sln,1075)$	(1) ΔH_{ds} YVO_4	94.8 ± 2.02
$Y_2O_3(s,298) \rightarrow Y_2O_3(sln,1075)$	(2) ΔH_{ds} Y_2O_3	32.8 ± 0.80
$V_2O_5(s,298) \rightarrow V_2O_5(sln,1075)$	(3) ΔH_{ds} V_2O_5	-15.92 ± 0.45
$2Y(s,298) + 3/2\ O_2(298,g) \rightarrow Y_2O_3(s,298)$	(4) $\Delta H^\circ_{f,el}$ Y_2O_3	-1905.3 ± 2.3[a]
$2V(s,298) + 5/2\ O_2(g,298) \rightarrow V_2O_5(s,298)$	(5) $\Delta H^\circ_{f,el}$ V_2O_5	-1550.59[b]
$1/2\ Y_2O_3(s,298) + 1/2\ V_2O_5(s,298) \rightarrow YVO_4(s,298)$ $\Delta H(6) = -\Delta H(1) + 1/2\ \Delta H(2) + 1/2\ \Delta H(3)$	(6) $\Delta H^\circ_{f,ox}$ YVO_4	-97.53 ± 1.52
$Y(s,298) + V(s,298) + 2O_2\ (g,298) \rightarrow YVO_4\ (s,298)$ $\Delta H(7) = 1/2\ \Delta H(4) + 1/2\ \Delta H(5) + \Delta H(6)$	(7) $\Delta H^\circ_{f,el}$ YVO_4	-1839.23 ± 1.91
$CeVO_4(s,298) + 1/4 O_2(g,1075) \rightarrow CeO_2(sln,1075) + 1/2 V_2O_5(sln,1075)$	(1)ΔH_{ds} $CeVO_4$	97.69 ± 1.88
$CeO_2(s,298) \rightarrow CeO_2(sln,1075)$	(2) ΔH_{ds} CeO_2	83.34 ± 1.86
$V_2O_5(s,298) \rightarrow V_2O_5(sln,1075)$	(3) ΔH_{ds} V_2O_5	-15.92 ± 0.45
$O_2(g,298) \rightarrow O_2(g,1075)$	(4) $\Delta H_{(298-975)}O_2$	21.74[c]
$Ce(s,298) + O_2(g,298) \rightarrow CeO_2(s,298)$	(5) ΔH°_f CeO_2	-1088.7 ± 1.5[c]
$2Ce(s,298) + 3/2 O_2(g,298) \rightarrow Ce_2O_3(s,298)$	(6) ΔH°_f Ce_2O_3	-1796.2 ± 8.4[d]
$2V(s,298) + 5/2\ O_2(g,298) \rightarrow V_2O_5(s,298)$	(7) ΔH°_f V_2O_5	-1550.59[c,e]
$1/2\ Ce_2O_3(s,298) + 1/2\ V_2O_5(s,298) \rightarrow CeVO_4(s,298)$ $\Delta H(8) = -\Delta H(1) + \Delta H(2) + 1/2\ \Delta H(3) - 1/4\ \Delta H(4) + \Delta H(5) - 1/2\ \Delta H(6)$	(8)$\Delta H^\circ f,ox CeVO_4$	-202.43 ± 5.18
$Ce(s,298) + V(s,298) + 2O_2(g,298) \rightarrow CeVO_4(s,298)$ $\Delta H(9) = -\Delta H(1) + \Delta H(2) + 1/2\Delta H(3) - 1/4\Delta H(4) + \Delta H(5) + 1/2\Delta H(7)$	(9)$\Delta H^\circ f,el CeVO_4$	-1875.02 ± 3.04

s, solid; g, gas; sln, solution in $2PbO \cdot B_2O_3$ at 1075 K.
[a] From [30].
[b] From [31].
[c] From [32].
[d] from [30].
[e] from [31].

thermochemical cycles used in the calculations are presented in Table 3. The thermochemical cycle for $CeVO_4$ is presented separately because previous experiments [26] showed that Ce^{3+} readily and completely oxidizes to Ce^{4+} during dissolution in the presence of oxygen. This is confirmed by its much more exothermic enthalpy of drop solution than that expected from the general trend (see Fig. 1). All other RE, including Tb, dissolve as trivalent ions [27]. The enthalpies of drop solution as a function of the RE ionic radii are presented in Fig. 1, and the enthalpies of formation from oxides vs. the RE ionic radii are shown in Fig. 2.

The accuracy in calorimetric measurements is typically ± 5 to $\pm 2\%$ depending on the magnitude of the heat effect and the chemistry of the samples. The accuracy of the heats of formation is typically ± 1 to ± 5 kJ/mol when errors are propagated through the thermochemical cycles to obtain enthalpies of formation from oxides. Enthalpies of formation of binary oxides from elements were taken from the literature and the final enthalpy of formation from elements includes these propagated errors.

4. Discussion

The enthalpies of formation of the vanadates can be compared with those of the phosphates [25] and tantalates and niobates [28] measured previously. With increasing
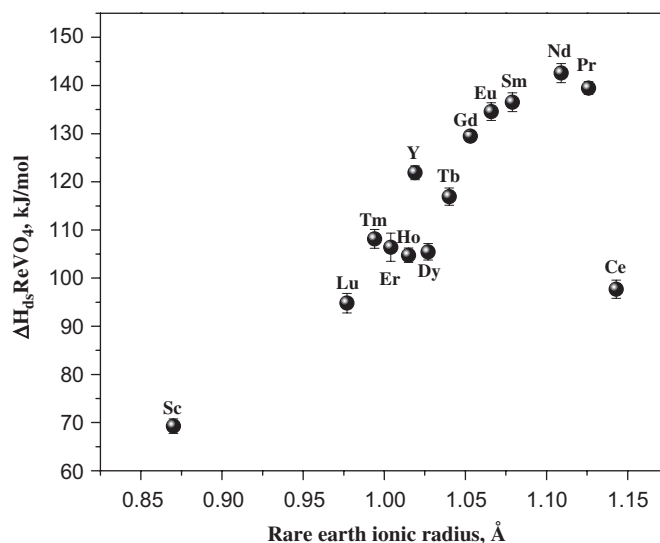

Fig. 1. Enthalpies of drop solution of $REVO_4$ compounds at 1075 K vs. RE^{3+} ionic radius.

RE^{3+} ionic radius, the stability of the $REPO_4$ (RE = Sc, Y, La–Nd, Sm–Lu) increases from $LuPO_4$ to $LaPO_4$ with respect to sesquioxides and phosphorus pentoxide (see Fig. 2). The vanadates follow a parallel trend but have less exothermic energies of formation from the oxides than the
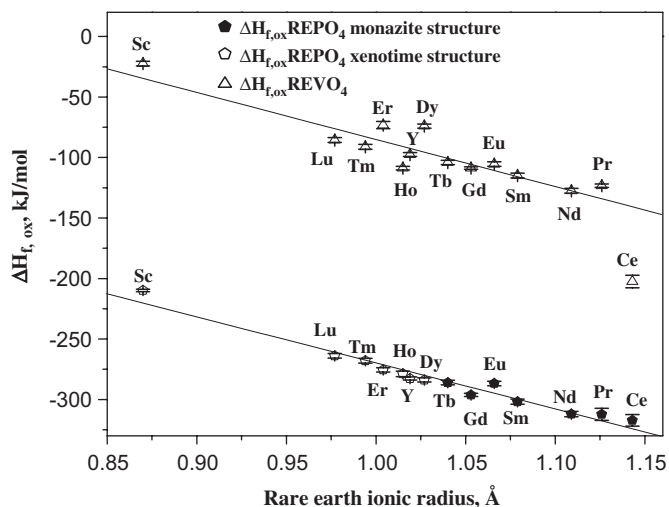
Fig. 2. Comparison of enthalpies of formation from oxides at 298 K for $REVO_4$ [this work] and $REPO_4$ compounds [25] vs. RE^{3+} ionic radius. Filled symbols indicate scheelite structure, open symbols zircon structure.

phosphates, reflecting the lower acidity of V_2O_5 relative to P_2O_5. The slopes of the two trends are similar. The phosphates crystallize in the zircon and/or scheelite (monazite) structure, while the vanadates are all zircon type. The earlier work [22] showed that the enthalpy of formation of phosphates fell on a single linear trend with ionic radius despite the existence of two different structures, implying small enthalpy differences between the structures. The parallel trend for zircon type vanadates seen for all rare earths studied (including those for which the phosphate is scheelite type) supports this conclusion.

The values for tantalates and niobates [28] seem very different from those for vanadates and phosphates, in particular showing the opposite trend with RE ionic radius. Our experience with ternary oxides of Nb and Ta shows them to be very refractory and difficult to dissolve in any solvents other than molten oxides. Thus it is not clear whether the different trends seen reflect experimental difficulties or real thermodynamic differences.

The newly obtained enthalpies of formation from elements generally fall closer to those calculated from equilibrium oxygen pressure data [21] than from thermal analysis (compare Tables 1 and 2). The thermal analysis values often appear lower in magnitude, perhaps suggesting incomplete reaction. We suggest that the new values, obtained directly by a well-established technique and using high quality samples, are reliable.

5. Conclusions

Enthalpies of formation from oxides and from elements were determined for 14 lanthanide vanadates. The data show that the enthalpies of formation of the $REVO_4$ become more negative with increasing RE ionic radius, confirming the increasing stability of these compounds. The trend is almost linear and is similar to that found previously for the rare earth phosphates. The vanadates are less stable relative to the oxide components and to elements, than are the corresponding rare earth phosphates.

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