

Lattice Enthalpies of Lanthanide Orthovanadates LnVO_4

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Abstract. Lattice enthalpies $\Delta_L H^\circ$ of lanthanide orthovanadates, LnVO_4 ($\text{Ln} = \text{Ce} - \text{Lu}$, except Pm) have been determined from the Born-Haber thermochemical cycle and compared with those calculated by an empirical equation. Two different sets of enthalpies of formation of LnVO_4 , from oxides (Ln_2O_3 , V_2O_5) and from elements, have been used but the differences in $\Delta_L H^\circ$ are small. The Born-Haber cycle in both routes yields close values of $\Delta_L H^\circ$ to those obtained after an empirical equation proposed by Glasser and Jenkins. It has been found that the partial derivative of the lattice enthalpies to the molar volumes corresponds by magnitude and dimension to the shear moduli of these crystals. (doi: [10.5562/cca2298](http://dx.doi.org/10.5562/cca2298))

Keywords: lattice enthalpies, lanthanide orthovanadates, shear moduli, thermochemistry, Born-Haber cycle

INTRODUCTION

Lanthanide orthovanadates, LnVO_4 ($\text{Ln} = \text{Ce} - \text{Lu}$) exhibit valuable catalytic, electric, magnetic and optical properties. Recent experimental studies comprise, *e.g.* photoconversion of cyclohexane and benzene by LnVO_4 ($\text{Ln} = \text{Ce, Pr, Nd}$),¹ visible-light photocatalysis by NdVO_4 nanowires,² laser applications and optoelectronic characteristics,^{3–5} electronic, mechanical and optical properties of GdVO_4 ,⁶ charge-transfer transitions in LnVO_4 ($\text{Ln} = \text{Gd, Lu}$): Eu^{3+} ,⁷ electronic structure of CeVO_4 from diffuse reflectance spectroscopy.⁸ Theoretical studies deal with magnetic properties of LnVO_4 ($\text{Ln} = \text{Eu, Ho, Lu}$),⁹ phase analyses of DyVO_4 ,¹⁰ band structure calculations of CeVO_4 ,⁸ local spin densities and band structure of GdVO_4 .⁶ LnVO_4 crystallize in zircon-type (ZrSiO_4) structure with $I4_1/\text{amd}$ space group (No. 141) and four molecules per unit cell;¹¹ they melt at high temperature, $T_m = 1710\text{--}2100\text{ K}$.¹²

The thermodynamic assessment of lanthanide orthovanadates is incomplete, although, *e.g.* five different sets exist in the changes of the standard enthalpy (CSE) of formation with values varying about 50 kJ mol⁻¹ for SmVO_4 .^{13,14} In Ref. 13, CSE of formation of LnVO_4 ($\text{Ln} = \text{Ce} - \text{Lu}$, except Pm, Yb) from oxides and from elements have been determined at $T = 298.15\text{ K}$ and at $T = 1075\text{ K}$ in solvent of lead borate ($2\text{PbO}\times 2\text{B}_2\text{O}_3$). Bond energies of LnVO_4 ($\text{Ln} = \text{Ce} - \text{Lu}$, except Pm) have been calculated using the dielectric chemical bond theory.¹⁵ In the same work, the whole

crystal of LnVO_4 is fragmented into a sum of binary crystals and only the energies of the bond types $\text{Ln}-\text{O}$, $\text{Ln}-\text{O}'$, and $\text{V}-\text{O}$ have been presented. The single prime ('') indicates different bond length with the cluster LnO_8' compared to LnO_8 .

The amount of energy per mole that binds the ions in the crystal lattice of LnVO_4 is among the basic characteristics of these compounds. The aim of the present work is to determine the lattice enthalpies of LnVO_4 by the Born-Haber thermochemical cycle and to relate these quantities to certain mechanical properties.

METHOD

The lanthanide orthovanadates LnVO_4 have a defined stoichiometry and the lattice is assumed to contain ions with integral charges. Therefore, the lattice enthalpies $\Delta_L H^\circ$ can be found by the Born-Haber cycle in Eq. (1) below. The term B corresponds to two different CSE of formation of LnVO_4 included in the cycle - from oxides or from elements (Eq. (2)):

$$\begin{aligned} B + \Delta_s H^\circ(\text{Ln}) + \Delta_s H^\circ(\text{V}) + 2\Delta_d H^\circ(\text{O}-\text{O}) + \Delta_i H^\circ(\text{Ln}) + \\ + \Delta_i H^\circ(\text{V}) + 4\Delta_{eg} H^\circ(\text{O}) - \Delta_L H^\circ(\text{LnVO}_4) = 0 \end{aligned} \quad (1)$$

$$B = \left[\Delta_{f,\text{ox}} H^\circ(\text{LnVO}_4) - \frac{1}{2} \Delta_f H^\circ(\text{Ln}_2\text{O}_3) - \frac{1}{2} \Delta_f H^\circ(\text{V}_2\text{O}_5) \right],$$

$$\text{or } B = \left[-\Delta_{f,\text{el}} H^\circ(\text{LnVO}_4) \right], \quad (2)$$

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Table 1. Born-Haber cycle for lanthanide orthovanadates, LnVO_4

No	Equation of the process in each step	ΔH°
1a.	$\text{LnVO}_4(\text{s}) \rightarrow (1/2)\text{Ln}_2\text{O}_3(\text{s}) + (1/2)\text{V}_2\text{O}_5(\text{s})$	$-\Delta_{\text{f, ox}}H^\circ$
1b.	$(1/2)\text{Ln}_2\text{O}_3(\text{s}) + (1/2)\text{V}_2\text{O}_5(\text{s}) \rightarrow \text{Ln}(\text{s}) + \text{V}(\text{s}) + 2\text{O}_2(\text{g})$	$-(1/2)\Delta_{\text{f}}H^\circ((\text{Ln}_2\text{O}_3), (\text{V}_2\text{O}_5))$
1.	$\text{LnVO}_4(\text{s}) \rightarrow \text{Ln}(\text{s}) + \text{V}(\text{s}) + 2\text{O}_2(\text{g})$	$-\Delta_{\text{f, el}}H^\circ$
2.	$\text{Ln}(\text{s}) + \text{V}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{Ln}(\text{g}) + \text{V}(\text{s}) + 2\text{O}_2(\text{g})$	$\Delta_sH^\circ(\text{Ln})$
3.	$\text{Ln}(\text{g}) + \text{V}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{Ln}(\text{g}) + \text{V}(\text{g}) + 2\text{O}_2(\text{g})$	$\Delta_sH^\circ(\text{V})$
4.	$\text{Ln}(\text{g}) + \text{V}(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{Ln}(\text{g}) + \text{V}(\text{g}) + 4\text{O}(\text{g})$	$2\Delta_dH^\circ(\text{O}_2)$
5.	$\text{Ln}(\text{g}) + \text{V}(\text{g}) + 4\text{O}(\text{g}) \rightarrow \text{Ln}^{3+}(\text{g}) + 3\text{e}^- + \text{V}(\text{g}) + 4\text{O}(\text{g})$	$\Delta_iH^\circ(\text{Ln})$
6.	$\text{Ln}^{3+}(\text{g}) + 3\text{e}^- + \text{V}(\text{g}) + 4\text{O}(\text{g}) \rightarrow \text{Ln}^{3+}(\text{g}) + 3\text{e}^- + \text{V}^{5+}(\text{g}) + 5\text{e}^- + 4\text{O}(\text{g})$	$\Delta_iH^\circ(\text{V})$
7.	$\text{Ln}^{3+}(\text{g}) + \text{V}^{5+}(\text{g}) + 4\text{O}(\text{g}) + 8\text{e}^- \rightarrow \text{Ln}^{3+}(\text{g}) + \text{V}^{5+}(\text{g}) + 4\text{O}^{2-}(\text{g})$	$4\Delta_{\text{eg}}H^\circ(\text{O})$
8.	$\text{Ln}^{3+}(\text{g}) + \text{V}^{5+}(\text{g}) + 4\text{O}^{2-}(\text{g}) \rightarrow \text{LnVO}_4(\text{s})$	$-\Delta_LH^\circ$

where the notation is as follows:¹⁶ the left-hand side subscript to each enthalpy refers to, respectively: L - lattice, f - formation, f, ox - formation from oxides, f, el - formation from elements, s - sublimation, i - ionization, d - dissociation, and eg - electron gain; the right-hand side superscript ($^\circ$) indicates “under standard conditions”: temperature $T = 298.15$ K, pressure $p = 101325$ Pa. The CSE are related to the corresponding energies of dissociation, electron gain, ionization, sublimation, and potential energy of the lattice according to the formulae, respectively:

$$\begin{aligned}\Delta_dH^\circ &= -\Delta_dU^\circ - \frac{5}{2}RT, \\ \Delta_{\text{eg}}H^\circ &= -(\Delta_{\text{eg}}U^\circ - 5RT), \\ \Delta_iH^\circ &= \Delta_iU^\circ + n\frac{5}{2}RT, \quad n = 3 \text{ for Ln, or } n = 5 \text{ for V}, \\ \Delta_sH^\circ &= \Delta_sU^\circ + \frac{5}{2}RT; \\ \text{LnVO}_4(\text{s}) &\rightarrow \text{Ln}^{3+}(\text{g}) + 4\text{O}^{2-}(\text{g}), \\ \Delta n(\text{g}) &= +6 \text{ mol}; \quad \Delta_LH^\circ = -\Delta_LU^\circ - 3RT.\end{aligned}\quad (3)$$

The input data for the calculation of Δ_LH° are presented in Table 2 and Table 3. The equation of each step (physical or chemical change) of the cycle is given in

Table 2. Standard enthalpy changes of vanadium and oxygen

$\Delta H^\circ / \text{kJ mol}^{-1}$	Value
$\Delta_iH^\circ(\text{V})$	$15729.9 \pm 1.2^{\text{(a)}}$
$\Delta_fH^\circ(\text{V}_2\text{O}_5)$	$-1550.6^{\text{(a)}}$
$\Delta_sH^\circ(\text{V})$	$515.8 \pm 0.1^{\text{(b)}}$
$\Delta_dH^\circ(\text{O}_2)$	$498.36 \pm 0.17^{\text{(a)}}$
$\Delta_{\text{eg}}H^\circ(\text{O})$	$715.4^{\text{(c)}}$

Data taken from: ^(a) Ref. 17; ^(b) Ref. 18; ^(c) Ref. 16.

Table 1. The sign of the CSE must be reversed if the actual processes take place in the opposite direction. The overall sum of CSE is equal to zero for a closed path of changes starting and ending at the same state. Here, the final step is the formation of lanthanide orthovanadate in solid phase, $\text{LnVO}_4(\text{s})$, from a gas of separated ions. This process is reverse to that one in the definition of lattice energy as displayed in the last row of Eq. (3).

RESULTS AND DISCUSSION

The lattice enthalpies obtained in this work are presented in Table 4. The values of the CSE of LnVO_4 lattice determined by the Born-Haber thermochemical cycle vary in a narrow range, about 1.1–1.4 % within the lanthanide series to the mean value, respectively for those determined from CSE of formation of LnVO_4 from oxides or from elements.

The Born-Haber cycle presented in Table 1 may start with either steps 1a and 1b (reverse process of the formation of LnVO_4 from oxides) or with step 1 (reverse process of the formation of LnVO_4 from elements) and then to proceed further via step 2, etc. The values of $-\Delta_{\text{f, el}}H^\circ$ ¹⁴ have been used in this study since they comprise all LnVO_4 except PmVO_4 .

The range of Δ_LH° variation is small as the formation of LnVO_4 is determined mainly by the change of Ln^{3+} ionic radii appropriate to the zircon structure and by the ionic $\text{Ln}-\text{O}$ bonds.⁹ The accuracy of each lattice enthalpy Δ_LH° has been evaluated with the aid of the available accuracies of the quantities included in Eq. (1). Since the uncertainties for some quantities in Table 2 are not available, the RMS deviations of Δ_LH° determined in this work should not be lower than 0.1 %.

Δ_LH° in this work are compared in Table 4 with an empirical equation for lattice potential energy Δ_LU (or U_{POT}).¹⁹ The equation has the following form:

Table 3. Standard enthalpy changes of formation of lanthanide orthovanadates and sesquioxides, and of sublimation and ionization of lanthanide metals (all in kJ mol^{-1})

LnVO_4	$-\Delta_{\text{f},\text{el}}H^\circ$ ^(a)	$-\Delta_{\text{f},\text{ox}}H^\circ$ ^(b)	$-\Delta_{\text{f}}H^\circ(\text{Ln}_2\text{O}_3)$ ^(c)	$\Delta_{\text{s}}H^\circ(\text{Ln})$ ^(c)	$\Delta_{\text{i}}H^\circ(\text{Ln})$ ^(d)
CeVO_4	1820.4	202.4 ± 5.2	1796.2	422.6	3541.7 ± 9.9
PrVO_4	1821.0	123.3 ± 1.4	1809.6	355.6	3646.1 ± 9.9
NdVO_4	1815.2	127.5 ± 2.0	1807.9	327.6	3715.8 ± 38.6
SmVO_4	1814.5	114.9 ± 1.9	1823.0 ± 3.0	206.7	3887.7 ± 38.6
EuVO_4	1729.3	105.4 ± 1.9	1651.4 ± 12.1	175.3	4054.3 ± 10.9
GdVO_4	1810.6	105.4 ± 1.9	1819.6 ± 12.1	397.5	3768.1 ± 19.3
TbVO_4	1826.0	104.2 ± 1.8	1865.2 ± 7.5	388.7	3808.7 ± 19.3
DyVO_4	1818.2	74.0 ± 1.7	1863.1 ± 7.5	290.4	3916.3 ± 37.4
HoVO_4	1823.3	108.8 ± 1.5	1880.7 ± 4.8	300.8	3941.5 ± 19.3
ErVO_4	1827.8	73.2 ± 2.9	1897.9 ± 1.9	317.1	3952.4 ± 19.3
TmVO_4	1819.2	91.1 ± 1.9	1888.7 ± 5.9	232.2	4062.7 ± 17.4
YbVO_4	1778.6	(88.4 ± 2.0)	1814.6	152.1	4212.6 ± 2.5
LuVO_4	1806.5	85.6 ± 2.0	1878.2	427.6	3905.5 ± 38.7

Data taken from: ^(a) Ref. 14; ^(b) Ref. 13; ^(c) Ref. 17; ^(d) Ref. 20.

$$U_{\text{POT}} = AI \left(\frac{2I}{v_m} \right)^{\frac{1}{3}} \quad (4)$$

where $A = 121.39 \text{ kJ mol}^{-1} \text{ nm}$ is an electrostatic factor, $I = 0.5 \sum n_i z_i^2$ is the ionic strength with n_i being the number of ions with charge z_i per formula, $I = 25$ for LnVO_4 , and v_m is the molecular volume in nm^3 . The necessary values of v_m are given in Table 4.

According to Eq. (3), both quantities $\Delta_L H^\circ$ and $\Delta_L U$ are related by factors proportional to $RT = 2.48 \text{ kJ mol}^{-1}$ at $T = 298.15 \text{ K}$, i.e. by 7.44 kJ mol^{-1} . The latter presents only 0.03 % of the value of $\Delta_L H^\circ$. The values in the last column of Table 4 determined by the empirical Eq. (4) are about 1–3 % lower than those yielded by the Born-Haber cycle. It has been indicated that the empirical formula used to obtain the last column in Table 4 results in estimates with certainty ± 7 % compared to the known values.¹⁹

Table 4. Molecular (v_m) and molar (V_m) volumes and lattice energies of lanthanide orthovanadates

LnVO_4	$v_m / 10^{-30} \text{ m}^3$	$V_m / 10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$\Delta_L H^\circ / \text{kJ mol}^{-1}$ this work ^(a)	$\Delta_L H^\circ / \text{kJ mol}^{-1}$ this work ^(b)	$\Delta_L U$ ^(c) / kJ mol^{-1}
CeVO_4	87.98	52.98	25944 ± 18	25889 ± 13	25137
PrVO_4	86.67	52.19	25909 ± 14	25927 ± 13	25263
NdVO_4	87.55	52.72	25954 ± 44	25963 ± 42	25178
SmVO_4	83.64	50.37	26000 ± 44	26013 ± 42	25565
EuVO_4	83.28	50.15	26040 ± 23	26063 ± 43	25602
GdVO_4	81.98	49.37	26063 ± 29	26080 ± 23	25736
TbVO_4	81.47	49.06	26114 ± 28	26127 ± 23	25790
DyVO_4	80.29	48.35	26092 ± 46	26129 ± 41	25915
HoVO_4	79.77	48.04	26171 ± 26	26170 ± 23	25972
ErVO_4	78.96	47.55	26171 ± 25	26201 ± 23	26060
TmVO_4	78.17	47.08	26210 ± 25	26218 ± 21	26148
YbVO_4	77.47	46.65	26221 ± 8	26247 ± 6	26226
LuVO_4	76.93	46.33	26237 ± 44	26244 ± 42	26287

^(a) Obtained with $\Delta_{\text{f},\text{ox}}H^\circ$.^(b) Obtained with $\Delta_{\text{f},\text{el}}H^\circ$.^(c) Determined after an empirical equation proposed by Glasser and Jenkins.¹⁹

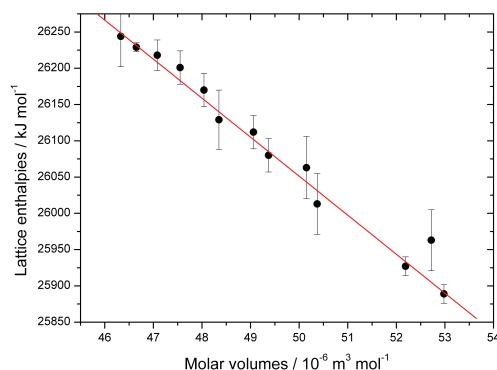


Figure 1. Variation of the lattice enthalpies vs. molar volumes of LnVO_4 .

A direct comparison of the lattice enthalpies obtained by the Born-Haber cycle reported here with those found by the dielectric chemical bond method¹⁵ is not possible since the latter contains only bond length energies. However, averaging the values for $\text{Ln}-\text{O}$ and $\text{Ln}-\text{O}'$ bonds, and after summation with the values for $\text{V}-\text{O}$ bonds, rough estimates of the lattice energies could be obtained, namely from 25763 kJ mol⁻¹ (CeVO_4) to 25969 kJ mol⁻¹ (LuVO_4), i.e. they are close to those in this work of Table 4.

It should be noted that the $\Delta_L H^\circ$ values reported here are derived from experimental values of CSE included in Eq. (1) and that they do not depend on possible mechanisms of summation of pair interactions, structural features, etc.

The plot of lattice enthalpies vs. molar volumes of LnVO_4 (with CSE of formation of LnVO_4 from elements) is presented in Figure 1. The straight line has a regression coefficient $R^2 = 0.9848$ and a negative slope $(\partial \Delta_L H^\circ / \partial V_m) = -51.71 \times 10^6 \text{ kJ m}^{-3}$, or $(\partial \Delta_L H^\circ / \partial V_m) = -51.71 \times 10^9 \text{ Pa}$. The negative sign of the slope accounts for the trend of changes of lattice enthalpies vs. molar volumes within the series of lanthanide orthovanadates. Thus, an upper limit for the shear modulus of LnVO_4 , $G = 51.7 \text{ GPa}$, has resulted in this case. The molar volumes V_m of LnVO_4 have been determined here by means of the corresponding densities from X-ray diffraction studies.²¹ Taking the molar volume of PmVO_4 as a mean value between those of NdVO_4 and SmVO_4 , the missing lattice enthalpy of PmVO_4 has been estimated, $\Delta_L H^\circ = 25979 \text{ kJ mol}^{-1}$.

It should be noted that the variation of the lattice enthalpies vs. molar volumes of LnVO_4 (with CSE of formation of LnVO_4 from oxides) results in similar straight line with slope $-48.02 \times 10^9 \text{ Pa}$ and a regression coefficient $R^2 = 0.9556$.

It is important to note that the novelty of the present study is equally based (except the lattice energies) on the physical meaning and dimension obtained from the slope $(\partial \Delta_L H^\circ / \partial V_m)$ since only this slope

preserves a correct shear modulus dimension: $[\text{J m}^{-3}] = [\text{Pa}]$. Any other linear plot, e.g. $\Delta_L H^\circ - v_m^{1/3}$ would result in dimension $[\text{N mol}^{-1}]$ and unclear physical meaning. Therefore, a possible improvement of the regression coefficient R^2 cannot be a priority task.

The slope $(\partial \Delta_L H^\circ / \partial V_m)$ and shear moduli have the same dimension [Pa]; it is reasonable that a displacement of ions can be related to shear modulus. The meaning of the slope is of an upper limit of energy that, after being absorbed, would result in lattice deformation. Recent measurements of the shear modulus of GdVO_4 by ultrasonic technique have revealed a value of $G = 40.5 \text{ GPa}$.⁶ The same authors have obtained theoretical values of $G = 49.8 \text{ GPa}$ or 53.0 GPa by two theoretical approximations. These results confirm an upper limit of the shear moduli $G \approx 50 \text{ GPa}$, an average value of both slopes, found in this work. The thermodynamic relations between the internal energy and the moduli of a solid are known at least for crystals of simple structure and small molar volumes.¹⁶

CONCLUSION

The lattice enthalpies $\Delta_L H^\circ$ of LnVO_4 increase slightly with increasing the atomic number in the lanthanide series and remain close to those determined by an empirically derived equation. The dependence between $\Delta_L H^\circ$ and molar volumes V_m is linear with a negative slope. The latter corresponds to lattice enthalpy per molar volume and can be considered as an upper limit of the shear moduli for the series of LnVO_4 .

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