Short communication

Lattice Enthalpies of Lanthanide Orthoferrites LnFeO$_3$

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Abstract

Lattice enthalpies $\Delta_L H^\Theta$ of lanthanide orthoferrites, LnFeO$_3$ have been determined by the Born-Haber cycle and compared with those calculated by an empirical equation. Enthalpies of formation of LnFeO$_3$ from two different sources have been employed: from oxides (Ln$_2$O$_3$, Fe$_2$O$_3$), for 12 LnFeO$_3$, and from elements, for 8 LnFeO$_3$, but the differences in $\Delta_L H^\Theta$ are very small. The Born-Haber cycle in both routes results in close values of $\Delta_L H^\Theta$ to those obtained by the empirical equation of Glasser and Jenkins. A correspondence in dimension and magnitude has been found between the partial derivative of the lattice enthalpies to the molar volumes and an upper limit of the shear moduli of the lanthanide orthoferrites.

Keywords: Lattice enthalpies; lanthanide orthoferrites; shear moduli; Born-Haber cycle

1. Introduction

Lanthanide orthoferrites, LnFeO$_3$ are members of the perovskites group ABX$_3$ and crystallize in an orthorhombic structure of space group Pbnm (No.62); each unit cell comprises four molecules (z = 4) with lanthanide and iron sites equivalent in symmetry.[1] Lanthanide orthoferrites, LnFeO$_3$ are among the most studied lanthanide solids. The continuing research interest is stimulated by a number of applications based on their valuable properties: magnetic, magneto-optical, sensing, catalytic, electrical, thermochemical, etc.

The magnetic properties of hydrothermally grown single-phase LnFeO$_3$ with all lanthanides Ln, except Ce and Pm, have been investigated recently and related to the Ln^{3+} ionic radii.[2] Spontaneous magnetostriction and thermal expansibility have been found in TmFeO$_3$ at low temperatures,[3] while SmFeO$_3$ exhibits temperature-induced magnetization reversal below the critical low temperature.[4] Low-temperature magnetic phase transitions in HoFeO$_3$ have been related to heat-capacity anomalies.[5]

Thick films of p-type semiconducting LnFeO$_3$, Ln = La or lanthanides from Pr to Lu, except Pm, have been prepared by polyol synthesis and tested in respect to gas sensing.[6] Lanthanide orthoferrites, LnFeO$_3$, Ln = Sm, Nd, Gd, have been synthesized as nanoparticles with size less than 150 nm,[7] as ceramic fibres with Ln = La, Sm, Gd, Dy, Er, Yb[8] or from molten NaOH flux with Ln = La, Pr, Nd.[9]

LnFeO$_3$ have been found effective as pigments, with Ln = La, Gd, Tm, Yb, Lu,[10] or as nanosize catalysts (Ln = La, Sm) in the photodegradation of rhodamine B under visible light.[11] Pressure and gamma sensing properties of substituted orthoferrites, Ln$_{0.7}$Ca$_{0.3}$FeO$_3$ (Ln = La, Gd, Dy, Y, Er) have been related to dc/ac resistivity and magnetic susceptibility.[12] Recent study of polycrystalline Mn-doped PrFeO$_3$ has been directed to structural, optical and dielectric properties.[13]

While the studies of the abovementioned properties are extensive and large in number, those on the thermodynamic properties are rare and do not cover the entire lanthanide series of orthoferrites. For example, nine thermodynamic functions have been generated from differential scanning calorimetry and solid-state electrochemical cells of LnFeO$_3$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er).[14,15] The changes of the standard enthalpies of formation (CSE) for twelve LnFeO$_3$, excluding those of Ce and Pm, and four reactions pertaining to the stability of lanthanide perovskites have been discussed on the basis of high-temperature (977 K) calorimetry using 2PbO.B$_2$O$_3$ flux.[16]

Various authors relate different energy characteristics of lanthanide orthoferrites to structural stability and physical properties. The standard free-energy change $\Delta_r G^\Theta$ for the reaction of formation of LnFeO$_3$ has been related to the Madelung energy;[17] *ab initio* calculated energy differences for LnFeO$_3$ have been assigned to the antiferromagnetic and ferromagnetic alignments between the iron

ions;[18] it has been observed a dependence between M–O bond energies and gas sensitivity of $LnMO_3$ (M = Cr, Fe).[6]

The energetics of the lanthanide orthoferrites is important for their systematic studies, including thermodynamic stability. The amount of molar energy binding the ions in the crystalline $LnFeO_3$ is a basic quantity for this series of compounds. In this paper we follow our research interest in the lattice enthalpies of various groups of lanthanide compounds, namely: $LnAlO_3$,[19] $Ln_3Ga_5O_{12}$,[20] $LnVO_4$,[21] and $LnPO_4$.[22] The purpose of this work is to determine the lattice energies of $LnFeO_3$ by the Born-Haber cycle and to relate the results to certain mechanical properties.

2. Method

The lanthanide orthoferrites, $LnFeO_3$ exhibit a defined stoichiometry and it is assumed that the lattice is built up of ions with integral charges. Hence, the lattice enthalpies $\Delta_L H^\theta$ can be determined by the Born-Haber cycle expressed in Eq. (1) below. The term A corresponds to two different CSE of formation of $LnFeO_3$ – either from oxides or from elements (Eq. (2)):

$$A + \Delta_s H^\theta(Ln) + \Delta_s H^\theta(Fe) + (3/2)\,\Delta_d H^\theta(O\text{–}O) + \\ + \Delta_i H^\theta(Ln) + \Delta_i H^\theta(Fe) + 3\Delta_{eg} H^\theta(O) - \\ - \Delta_L H^\theta(LnFeO_3) = 0, \quad (1)$$

$$A = [-\Delta_{f,ox} H^\theta(LnFeO_3) - (1/2)\Delta_f H^\theta(Ln_2O_3) - \\ (1/2)\Delta_f H^\theta(Fe_2O_3)], \quad (2) \\ \text{or } A = [-\Delta_{f,el} H^\theta(LnFeO_3)],$$

where the notation is as follows:[23] the left-hand side subscript to each enthalpy refers to, respectively: L-lattice, f–formation, f,el-formation from elements, f,ox-formation from oxides, s-sublimation, i-ionization, d-dissociation, and eg-electron gain; the superscript ($^\theta$) designates "standard conditions": temperature T = 298.15 K, pressure P = 101325 Pa. The CSE are related to the corresponding energies of dissociation, electron gain, ionization, subli-

mation, and potential energy of the lattice according to the formulae, respectively:

$$\Delta_d H^\theta = -\Delta_d U^\theta - (5/2)RT, \Delta_{eg} H^\theta = \\ = \Delta_{eg} U^\theta - 5RT, \Delta_i H^\theta = \Delta_i U^\theta + 3(5/2)RT, \quad (3)$$

$$\Delta_s H^\theta = \Delta_s U^\theta + (5/2)RT; \quad (4)$$

$$LnFeO_3(s) \rightarrow Ln^{3+}(g) + Fe^{3+}(g) + \\ + 3\ O^{2-}(g), \Delta n(g) = + 5\ \text{mol}; \Delta_L H^\theta = \quad (5) \\ = -\Delta_L U^\theta - 3RT.$$

The necessary data for the calculation of $\Delta_L H^\theta$ are presented in Table 2 and Table 3. The equation for each step (physical or chemical change) of the cycle is presented in Table 1. The sign of each CSE must be reversed if the actual process takes place in the opposite direction. The sum of all CSE is equal to zero for a closed route of changes starting and ending at one and the same state. Here, the final process is the formation of lanthanide orhoferrites in solid phase, $LnFeO_3(s)$, from ions in gas phase. This step is reverse to that one in the definition of lattice energy as displayed in Eq. (5).

3. Results and Discussion

The lattice enthalpies obtained in this work are presented in Table 4. The values of $\Delta_L H^\theta$ of lanthanide orhoferrite lattice determined by the Born-Haber thermochemical cycle vary slightly, 2.1 or 2.4 % within the lanthanide series to the mean value, respectively for those determined with CSE of formation of $LnFeO_3$ from elements or from oxides.

The Born – Haber cycle displayed in Table 1 begins with either steps 1a and 1b (reverse process of the formation of $LnFeO_3$ from oxides) or with step 1 (reverse process of the formation of $LnFeO_3$ from elements) and then to proceed via steps 2 to 8. The reported values of $\Delta_{f,ox} H^\theta$ [16] have been used in the first route and of $\Delta_{f,el} H^\theta$ [15] in the second one.

Table 1. Born – Haber cycle for lanthanide orthoferrites, $LnFeO_3$

No	Equation of the process in each step	ΔH^θ
(1a.	$LnFeO_3(s) \rightarrow (1/2)Ln_2O_3(s) + (1/2)Fe_2O_3(s)$	$-\Delta_{f,ox} H^\theta$
1b.	$(1/2)Ln_2O_3(s) + (1/2)Fe_2O_3(s) \rightarrow Ln(s) + Fe(s) + (3/2)O_2(g)$	$-(1/2)\Delta_f H^\theta$
		$(Ln_2O_3), (Fe_2O_3))$
1.	$LnFeO_3(s) \rightarrow Ln(s) + Fe(s) + (3/2)O_2(g)$	$-\Delta_{f,el} H^\theta$
2.	$Ln(s) + Fe(s) + (3/2)O_2(g) \rightarrow Ln(g) + Fe(s) + (3/2)O_2(g)$	$\Delta_s H^\theta(Ln)$
3.	$Ln(g) + Fe(s) + (3/2)O_2(g) \rightarrow Ln(g) + Fe(g) + (3/2)O_2(g)$	$\Delta_s H^\theta(Fe)$
4.	$Ln(g) + Fe(g) + (3/2)O_2(g) \rightarrow Ln(g) + Fe(g) + 3O(g)$	$(3/2)\Delta_d H^\theta(O_2)$
5.	$Ln(g) + Fe(g) + 3O(g) \rightarrow Ln^{3+}(g) + 3e^- + Fe(g) + 3O(g)$	$\Delta_i H^\theta(Ln)$
6.	$Ln^{3+}(g)+3e^-+Fe(g)+3O(g)\rightarrow Ln^{3+}(g)+3e^-+Fe^{3+}(g)+3e^-+3O(g)$	$\Delta_i H^\theta(Fe)$
7.	$Ln^{3+}(g)+Fe^{3+}(g)+3O(g)+6e^- \rightarrow Ln^{3+}(g)+Fe^{3+}(g)+3O^{2-}(g)$	$3\Delta_{eg} H^\theta(O)$
8.	$Ln^{3+}(g) + Fe^{3+}(g) + 3O^{2-}(g) \rightarrow LnFeO_3(s)$	$-\Delta_L H^\theta$

The range of $\Delta_L H^\Theta$ variation is small since the formation of $LnFeO_3$ is determined mainly by the change of Ln^{3+} ionic radii appropriate to the perovskite structure, i.e. by the ionic Ln – O bonds. The accuracies of determination of $\Delta_L H^\Theta$ have been evaluated with the accuracies of the quantities as included in Eq. (1) where available. Because of the lack of standard deviations for certain quantities in Table 2 and Table 3, the r.m.s. deviations of $\Delta_L H^\Theta$ determined in the present work should be considered minimal ones and not lower than 0.2% of the respective value. The r.m.s. deviations of $\Delta_L H^\Theta$ obtained from $\Delta_{f,el} H^\Theta$ are smaller because of the smaller number of terms included in the summation, Eqs. (1) and (2).

Table 2. Standard enthalpy changes of iron and oxygen

ΔH^Θ /kJ mol^{-1}	Value	Ref.
$\Delta_i H^\Theta(Fe)$	5300.4 ± 0.1	[24]
$\Delta_f H^\Theta(Fe_2O_3)$	-824.2	[24]
$\Delta_s H^\Theta(Fe)$	398.6 ± 0.1	[25]
$\Delta_d H^\Theta(O_2)$	498.36 ± 0.17	[24]
$\Delta_{eg} H^\Theta(O)$	715.4	[23]

$\Delta_L H^\Theta$ determined here are compared in Table 4 with an empirical equation for lattice potential energy $\Delta_L U$, i.e. U_{POT} [26]. The equation is as follows:

$$U_{POT} = A I \left(\frac{2I}{v_m} \right)^{1/3} \qquad (6)$$

where $A = 121.39$ kJ mol^{-1} nm (an electrostatic factor), $I = \frac{1}{2} \sum n_i z_i^2$ is the ionic strength with n_i being the number of ions with charge z_i per formula, $I = 15$ for $LnFeO_3$, and v_m is the molecular volume in nm^3; the corresponding values of v_m are given in Table 4.

According to Eq. (5), the quantities $\Delta_L H^\Theta$ and $\Delta_L U$ are related by factor proportional to RT = 2.48 kJ mol^{-1} at T=298.15 K, or by 7.44 kJ mol^{-1} with the inclusion of the zero-point energy.[27] This value presents about 0.05% of the value of $\Delta_L H^\Theta$.

The values in the last column of Table 4 determined by Eq. (6) are about 4% lower than those yielded by the Born – Haber cycle. It has been commented that the empirical formula (6) should yield estimates within $\pm$ 7% compared to the known values.[26]

It should be noted that the $\Delta_L H^\Theta$ values in the present work are obtained from experimental values of CSE included in Eq. (1) and that they do not depend on structural features or mechanisms of summation of pair interactions.

The plot of lattice enthalpies vs. molar volumes of $LnFeO_3$ (with CSE of formation of $LnFeO_3$ from oxides) is presented in Fig. 1. The straight line has a regression coefficient $R^2 = 0.981$ and a negative slope $(\partial \Delta_L H^\Theta / \partial V_m)$ = -127.0×10^6 kJ m^{-3}, or $(\partial \Delta_L H^\Theta / \partial V_m) = -127.0 \times 10^9$ Pa. The negative sign of the slope accounts for the trend of changes of lattice enthalpies within the series of 12 lanthanide orthoferrites.

Hence, an upper limit for the shear modulus of $LnFeO_3$, $G \approx 150$ GPa, has appeared in this case. The molar volumes V_m of $LnFeO_3$ have been determined here from the reported unit cell volumes.[2] Taking the molar volume of $PmFeO_3$ as a mean value between those of $NdFeO_3$ and $SmFeO_3$, 35.365×10^{-6} m^3 mol^{-1}, the missing lattice enthalpy of $PmFeO_3$ has been found, $\Delta_L H^\Theta = 14031$ kJ mol^{-1}.

The variation of the lattice enthalpies vs. molar volumes of $LnFeO_3$ with CSE of formation of $LnFeO_3$ from elements results in similar straight line with a regression coefficient $R^2 = 0.9602$ and negative slope, -128.1×10^9 Pa.

It is important to note that the novelty of the present study is equally based on the lattice enthalpies and on the

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

$LnFeO_3$	$-\Delta_{f,el} H^\Theta$ [15]	$-\Delta_{f,ox} H^\Theta$ [16]^a	$-\Delta_f H^\Theta(Ln_2O_3)$ [24]	$\Delta_s H^\Theta(Ln)$ [24]	$\Delta_i H^\Theta(Ln)$ [28]
$PrFeO_3$		48.53	1809.6	355.6	3646.1 ± 9.9
$NdFeO_3$	1357.4	44.35	1807.9	327.6	3715.8 ± 38.6
$SmFeO_3$	1355.2	44.35	1823.0 ± 3.0	206.7	3887.7 ± 38.6
$EuFeO_3$	1285.6	44.35	1651.4 ± 12.1	175.3	4054.3 ± 10.9
$GdFeO_3$	1360.5	44.35	1819.6 ± 12.1	397.5	3768.1 ± 19.3
$TbFeO_3$	1372.4	40.17	1865.2 ± 7.5	388.7	3808.7 ± 19.3
$DyFeO_3$	1369.4	35.98	1863.1 ± 7.5	290.4	3916.3 ± 37.4
$HoFeO_3$	1364.2	35.98	1880.7 ± 4.8	300.8	3941.5 ± 19.3
$ErFeO_3$	1400.5	35.98	1897.9 ± 1.9	317.1	3952.4 ± 19.3
$TmFeO_3$		27.61	1888.7 ± 5.9	232.2	4062.7 ± 17.4
$YbFeO_3$		23.43	1814.6	152.1	4212.6 ± 2.5
$LuFeO_3$		19.25	1878.2	427.6	3905.5 ± 38.7

^{a} all with r.m.s. devs.= $\pm$ 12.55 kJ mol^{-1};

Table 4. Molecular (v_m) and molar (V_m) volumes and lattice enthalpies of lanthanide orthoferrites

LnFeO$_3$	v_m/10^{-30} m^3	V_m/10^{-6} m^3 mol^{-1}	$\Delta_L H^\ominus$/ kJ mol^{-1} this work [a]	$\Delta_L H^\ominus$/ kJ mol^{-1} this work [b]	$\Delta_L U$ / kJ mol^{-1} [c]
PrFeO$_3$	59.35	35.74	13960 ± 24		14505
NdFeO$_3$	59.175	35.64	13997 ± 52	13994 ± 40	14519
SmFeO$_3$	58.275	35.09	14055 ± 54	14042 ± 40	14593
EuFeO$_3$	58.00	34.93	14104 ± 31	14108 ± 12	14616
GdFeO$_3$	57.775	34.79	14125 ± 39	14119 ± 20	14635
TbFeO$_3$	56.825	34.22	14175 ± 37	14163 ± 20	14716
DyFeO$_3$	56.75	34.18	14179 ± 55	14169 ± 38	14723
HoFeO$_3$	56.30	33.90	14223 ± 35	14199 ± 20	14762
ErFeO$_3$	56.025	33.74	14259 ± 34	14263 ± 20	14786
TmFeO$_3$	55.475	33.41	14272 ± 34		14835
YbFeO$_3$	55.275	33.29	14300 ± 16		14853
LuFeO$_3$	54.90	33.06	14296 ± 52		14886

[a] obtained with $\Delta_{f, ox}H^\ominus$,   [b] obtained with $\Delta_{f, el}H^\ominus$,   [c] determined after an empirical equation of Glasser and Jenkins [26]

physical meaning, dimension and magnitude obtained from the slope ($\partial \Delta_L H^\ominus / \partial V_m$); this slope retains a correct shear- modulus dimension: [J m^{-3}] = [Pa].
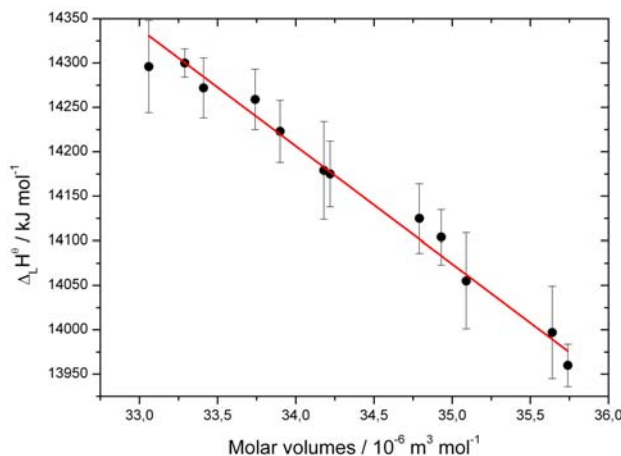
Figure 1. Variation of the lattice enthalpies vs. molar volumes of LnFeO$_3$ with enthalpies of formation of LnFeO$_3$ from oxides

The slope ($\partial \Delta_L H^\ominus / \partial V_m$) and shear moduli have the same dimension, [Pa]; it is obvious that a displacement of ions can be related to shear modulus. The meaning of the slope is of a critical amount of energy that, after being absorbed, will result in lattice destruction. Recent studies of the mechanical moduli of NdFeO$_3$ by equation of state V(P) in the Birch – Mournaghan form have revealed a value of E = 244 ± 4 GPa for the elastic (Young's) modulus [29] and K = 195.1 GPa [30] for the bulk modulus. From these experimental results we have calculated the value of the shear moduli G using the relationships between E, K, and G;[23] the obtained value is G = 94.5 GPa, which is lower than both slopes found in this work. Other reported values of mechanical moduli of LnFeO$_3$ are close to those for

NdFeO$_3$: for GdFeO$_3$, mean calculated bulk modulus K= 182 GPa,[31] and experimental K = 204.2 GPa.[30] The thermodynamic relations between the internal energy and the moduli of a solid have explicit forms only for crystals of simple structure and small molar volumes.[23]

4. Conclusions

The lattice enthalpies $\Delta_L H^\ominus$ of LnFeO$_3$ increase linearly with decreasing the molar volumes V$_m$ within the lanthanide series and remain close to those determined after an empirical equation. The negative slope of this dependence corresponds to lattice enthalpy per molar volume and can be considered as an upper limit of the shear moduli for the series of LnFeO$_3$. Similar relationships have been observed in our previous studies on lanthanide complex oxides.[19–22]

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6. References

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Povzetek

Z uporabo Born-Haberjevega ciklusa smo določili mrežne entalpije, $\Delta_L H^{\ominus}$, lantanoidnih ortoferitov, $LnFeO_3$, ter dobljene vrednosti primerjali s tistimi, dobljenimi z empiričnimi enačbami. Entalapije smo za 12 spojin določili s pomočjo podatkov za okside (Ln_2O_3, Fe_2O_3), za 8 spojin pa s pomočjo podatkov za elemente, vendar je razlika v $\Delta_L H^{\ominus}$ zelo majhna. Vrednosti, dobljene s pomočjo Born-Haberjevega ciklusa se dobro ujemajo s tistimi, izračunanimi z empiričnimi enačbami Glasserja in Jenkinsa. Ugotovili smo povezavo med dimenzijami ter parcialnimi odvodi mrežnih entalpij na parcialni molski volumen ter zgornjo limito strižnega modula proučevanih spojin.