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A comparison of methods for the estimation of the enthalpy of formation of rare earth compounds†

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Rare earth elements are helping drive the global transition towards a greener economy. However, the way in which they are produced is far from being considered green. One of the major obstacles to developing greener production methods and the design of novel processes and materials involving rare earth elements is the limited thermodynamic data available. In the present work, we apply a suite of methods to estimate the enthalpy of formation of several rare earth compounds, including a new method based on a linear relationship, established by the authors. Experimental values of the enthalpy of formation of $LnCl_3$, LnOCl, $LnPO_4$, Ln_2O_2S, $Ln_2O_2CO_3$ and $NaLnO_2$ were collated and used to assess the accuracy of the different methods, which were then used to predict values for compounds for which no data exists. It is shown that Mostafa *et al.*'s group contribution method and the linear relationship proposed by the authors give the lowest mean absolute error (<9%). The volume based thermodynamics (VBT) method yields estimates with absolute mean errors below 16.0% for $LnPO_4$ and Ln_2O_2S, but above 26.0% for other compounds. Correction of the VBT method using an improved estimate of the Madelung energy for the calculation of the lattice enthalpy decreases the absolute mean error below 12.0% for all compounds except $LnPO_4$. These complementary methods provide options for calculating the enthalpy of formation of rare earth compounds, depending on the experimental data available and desired accuracy.

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Introduction

Rare earth elements, commonly called the lanthanides (Ln), are playing a major role in the move towards a more sustainable society, due to their use in green technologies, including electric vehicles and wind turbines.[4,5] Rare earth oxycarbonates ($Ln_2O_2CO_3$) are important for manufacturing high-temperature superconductors, solid oxide fuel cells and permeable membranes; and as alternative catalysts for biodiesel production and dehydrogenation of primary aliphatic alcohols, due to their environmental benefits and process efficiency.[6–8] In addition, rare earth oxysulfides (Ln_2O_2S) are becoming important in the manufacture of red phosphors and oxygen storage, based on the reversible oxidation of sulphur to produce $Ln_2O_2SO_4$.[9–11] The use of rare earth elements in almost all of these applications is linked to their characteristic chemical, magnetic and electronic properties, making their substitution difficult.[12]

The applications discussed above, are pushing the global demand for rare earth compounds, increasing their beneficiation and extraction from ores and recycling from end-of-life products. The current chemical technologies used for extraction of rare earth elements have serious environmental impacts and are energy inefficient.[13,14] In view of this, industry is looking to design novel processes for their extraction and recovery.[15–19] For instance, in the early 80s high temperature reactions between Ln_2O_3 with different sodium compounds was studied, due to the formation of $NaLnO_2$ compounds affecting the swelling behavior of nuclear reactors during the cooling of liquid sodium;[20] a similar approach has been applied to recover REEs from waste fluorescent phosphors.[21,22] One of the main obstacles inhibiting the design of novel processing routes and synthesis of new rare earth element compounds is the lack of thermodynamic data available, because experimental measurements of their thermodynamic properties are extremely challenging.[23]

Knowledge of the enthalpies of formation of rare earth element compounds is crucial for calculations of Gibbs free energies and chemical equilibria. Methods exist for predicting

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these values, but some are only parameterised for a particular set of chemical compounds, while more general methods, based on group contribution, fail to provide a user-friendly mathematical model or the required data is only available for particular compounds of interest.[23,24] Other methods rely on the lattice potential energy, from the Born–Haber–Fajans cycle, to calculate enthalpies formation. Born-Lande developed in 1918 an equation to estimate lattice potential energies of binary ionic crystals which was further improved on by Born and Mayer. Kapustinskii developed the previous equations to allow calculation of the lattice potential energy of any simple ionic crystal.[25] Jenkins *et al.*[26,27] extended Kapustinskii's equation to link the lattice potential energy with the molecular volume of the crystal unit cell.

In view of this, in the present work, we evaluate a suite of methods for estimating the enthalpy of formation of rare earth compounds, using the rare earth oxides, phosphates, chlorides, oxychlorides, oxysulfides, oxycarbonates and sodium lanthanide oxides as a test set. In particular, we assess the performance of the volume based thermodynamic (VBT) method developed by Glasser and Jenkins[2,3] and group contribution method reported by Mostafa and Eakman,[1] which were chosen for their ease of use. In addition, we show, for the first time, that a linear relationship exists between $\Delta H_f^0(Ln_2O_3)$ and ΔH_f^0(LnSalt), where $\Delta H_f^0(Ln_2O_3)$ is the enthalpy of formation of the rare earth oxides (Ln_2O_3) and ΔH_f^0(LnSalt) is the enthalpy of formation of the rare earth salts under study. If experimental data is available for some rare earth compounds in the series, these can be used to easily estimate values for others.

Crystal structures

Before describing the methodology employed in this work, it is useful to provide a brief description of the crystal structures of the compounds considered.

Rare earth sesquioxides (Ln_2O_3)

Rare earth sesquioxides are polymorphic. At ambient conditions the cubic structure (form C, space group *Ia*3) is the most thermodynamically stable for all rare earth sesquioxides, with the exception of La_2O_3, Ce_2O_3 and Nd_2O_3.[28] In the cubic phase, the rare earth ions are six-coordinate and there are sixteen formula units per unit cell.[29,30] For La_2O_3, Ce_2O_3 and Nd_2O_3 a hexagonal structure (form A, space group *P*32/*m*) is observed.[29] In the hexagonal phase, the rare earth ions are seven-coordinate and there is one formula unit per unit cell. For the light rare earth elements, the thermochemical stability of forms A and C are similar, such that lanthanide sesquioxides with a mixture of both phases can be found at room temperature.[31]

Anhydrous rare earth trichlorides ($LnCl_3$)

Rare earth trichlorides are also polymorphic, presenting three structures at room temperature, depending on atomic number.[32] The trichlorides from $LaCl_3$ to $GdCl_3$ are isostructural, having a hexagonal UCl_3 structure (space group *P*63/*m*) in which rare earth ions are symmetrically coordinated to nine chloride ions.[33] The rare earth chlorides from $DyCl_3$ to $LuCl_3$ present a monoclinic YCl_3 structure (space group *C*2/*m*) in which the chloride ions are arranged in a nearly cubic close packed arrangement, with the rare earth ions located in the octahedral holes formed by alternate pairs of close packed layers of chloride ions.[34] $TbCl_3$ has the orthorhombic $PuBr_3$ structure (space group *Cmcm*), which can be described as triangular prisms in which Tb^{3+} is eight coordinated, with Tb^{3+} located at the center and Cl^- situated at the corners.[35] Rycerz and Gaune-Escard[36] investigated the correlation between the thermodynamic properties and crystal structure of rare earth trihalides, using differential scanning calorimetry. They found that $TbCl_3$ was the first compound of the series to present a solid–solid phase transition, pointing out that the structure of $TbCl_3$ depends on the methodology employed for its synthesis, being possible to obtain either the hexagonal (UCl_3) or orthorhombic ($PuBr_3$) structure. It is only possible to obtain the hexagonal form of $TbCl_3$, when it is prepared below 640 K.[36]

Rare earth oxychlorides (LnOCl)

Rare earth oxychlorides from LaOCl–HoOCl crystallize in the PbFCl tetragonal crystal structure (space group *P*4/*nmm*), meanwhile TmOCl–LuOCl adopt the SmSI hexagonal structure (space group *R*32/*m*). ErOCl is dimorphic and can present both structures. The change from tetragonal to hexagonal structure is due to the rearrangement of the chloride ions to reduce the strain present in the tetragonal form, when the ionic radius of the rare earth cation is small enough to allow it.[37,38]

Rare earth phosphates ($LnPO_4$)

Rare earth phosphates change crystal structure with increasing ionic radius. From $LaPO_4$ to $GdPO_4$ they adopt the monoclinic monazite structure (space group *P*21/*n*), while from $TbPO_4$ to $LuPO_4$ they adopt the tetragonal xenotime structure (space group *I*41/*amd*). Depending on preparation conditions, $GdPO_4$, $TbPO_4$ and $DyPO_4$ can adopt either structure.[39] Both structures contain isolated ${PO_4}^{3-}$ tetrahedral separated by LnO_9 polyhedra for monazite or LnO_8 polyhedra for xenotime structure.[40]

Ternary sodium lanthanide oxides ($NaLnO_2$)

All the sodium rare earth oxides have an ordered rocksalt lattice and can present three different crystal structures, depending on the relative size of the Na^+ and Ln^{3+}. If the Ln^{3+} ion is bigger than Na^+ (*i.e.* from La to Gd) the tetragonal α-$LiFeO_2$ structure (space group *I*4$_1$/*amd*) is found. If the Ln^{3+} is smaller than Na^+, two different structures are possible. The monoclinic β-$LiFeO_2$ structure (space group *C*2/*c*) is found from Tb to Er and the hexagonal α-$NaFeO_2$ structure (space group *R*3*m*) from Tm to Lu.[41,42] Impurities from other Ln^{3+} ions may alter the structure suggesting polymorphisms in the $NaLnO_2$ series.[20]

Lanthanide oxycarbonates ($Ln_2O_2CO_3$)

Rare earth oxycarbonates exists in three polymorphic crystalline structures. The tetragonal Type I structure has square ${Ln_2O_2}^{2+}$ layers separated by ${CO_3}^{2-}$ ions. The type IA is a monoclinic distortion of the type I. The type II structure has hexagonal $Ln_2O_2^{2+}$ layers separated by CO_3^{2-} ions.[7] The transformation of the type I to the type II structure has been observed for the light lanthanides at temperatures higher than 400 °C, whereas no type II structure has been reported for members beyond Gd.[43]

Lanthanide oxysulfides (Ln_2O_2S)

Rare earth oxysulfides have a trigonal crystal structure (space group *P*3*m*1), with one formula per unit cell. This structure is closely related with the A-type structure of the rare earth sesquioxides and can be described as an alternative stacking of $Ln_2O_2^{2+}$ and S^{2-} layers.[10,53,54]

Methodology

In this section we outline the various methods used for calculating enthalpies of formation. Example calculations, for $LaPO_4$, are given in the ESI.†

Experimental enthalpies of formation

A literature review of the experimental enthalpy of formation values of the different rare earth compounds considered in this work was carried out and their average values are presented in Table 1.

Group contribution method

Mostafa *et al.*[1] developed a group contribution (GC) method to estimate the enthalpy of formation (ΔH_f^0) of solid inorganic salts. It is based on a multiple linear regression analysis, which calculates the contribution of each cation, anion and ligand molecule to the total heat of formation of the inorganic solid. We used this method to estimate the enthalpy of formation of rare earth compounds using the values of the different ionic contributions in ref. 1. The contribution of the ion S^{2-} was estimated as the difference between the contribution of the ligand H_2S and two times the contribution of the ion H^+ giving a value of 108.8 kJ mol^{-1}.

Volume based thermodynamics

The volume based thermodynamics method (VBT), is a range of correlation methods that rely on the volume of the condensed phases to estimate thermodynamic properties.[2,3] This method was used to predict the lattice potential energy of rare earth compounds, which was input into the Born–Haber–Fajans cycle (BHFC) to calculate ΔH_f^0 from their individual elements. The lattice potential energy was calculated using the equations proposed by Jenkins and Glasser[55,56]

$$U_{POT} = 2I\left(\frac{\alpha}{V_m^{\frac{1}{3}}} + \beta\right) \quad (1)$$

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

where V_m is the molecular volume in nm^3 calculated from experimental X-ray diffraction data, α = 139.0 kJ mol^{-1} and β = 28.0 kJ mol^{-1} are empirical constants determined by statistical analysis of experimental data;[57] $I = 1/2\sum n_i z_i^2$ is the ionic strength factor, which is a summation over the product of the n_i ions with a charge of z_i for the different ionic constituents of the chemical formula; $A = \frac{1}{2}N_A M e^2/4\pi\varepsilon_0$ is a standard electrostatic constant with the value of 121.4 kJ mol^{-1}; N_A is Avogadro's number, M is the Madelung constant of sodium chloride; e the charge of an electron and $4\pi\varepsilon_0$ the vacuum permittivity. As recommended by Jenkins and Glasser,[55,56] for lattice energies below 5000.0 kJ mol^{-1}, eqn (1) was used, otherwise eqn (2) was used.

Since the BHFC is an enthalpy cycle, the lattice energy (U_{POT}) calculated using eqn (1) and (2) was transformed into lattice enthalpy[55] using the following expression

$$-\Delta H_L = U_{POT} + \sum_{i}^{\text{ions in formula unit}} s_i\left(\frac{c_i}{2} - 2\right)RT \quad (3)$$

where s_i is the number of ions of type i in the formula unit; c_i is a constant that takes a value of 3, 5 and 6 depending on

Table 1 Average experimental value of the enthalpy of formation (ΔH_f^0(LnSalt)) (kJ mol^{-1}) for the rare earth compounds considered in this study[39,44–52]

Ln	Ln_2O_3	$LnCl_3$	LnOCl	$LnPO_4$	$Ln_2O_2CO_3$[a]	Ln_2O_2S	$NaLnO_2$
La	−1793.8 ± 1.3	−1072.1 ± 0.9	−1013.8 ± 4.4	−1937.2 ± 47.4	−2388.4 ± 3.5	−1723.8 ± 9.3	u.k.
Ce	−1799.7 ± 7.1	−1056.0 ± 3.3	−1002.3 ± 2.4	−1949.8 ± 25.5	u.k.	−1743.0	−1127.0
Pr	−1812.6 ± 6.7	−1057.6 ± 1.0	−1013.6 ± 0.6	−1969.5	u.k.	−1742.4 ± 6.8	u.k.
Nd	−1808.2 ± 0.6	−1041.5 ± 0.4	−1000.5 ± 0.5	−1931.9 ± 51.7	−2382.1 ± 9.4	−1733.7 ± 19.1	u.k.
Pm	−1811.0	−1029.3	u.k.	u.k.	u.k.	−1751.4	u.k.
Sm	−1824.0 ± 1.7	−1026.4 ± 1.2	−994.9 ± 4.8	−1922.2 ± 61.6	u.k.	−1747.1 ± 18.0	u.k.
Eu	−1658.3 ± 6.0	−936.8 ± 1.5	u.k.	−1880.9 ± 14.5	−2202.4 ± 12.0	−1578.0 ± 19.5	u.k.
Gd	−1824.5 ± 10.6	−1007.3 ± 1.9	−980.8 ± 2.5	−1924.6 ± 53.2	u.k.	−1744.2 ± 28.0	u.k.
Tb	−1865.4 ± 0.0	−1000.1 ± 4.6	−981.8 ± 5.5	−1947.8 ± 38.2	u.k.	−1762.9 ± 13.5	u.k.
Dy	−1863.3 ± 0.6	−996.6 ± 4.9	−986.3 ± 2.5	−1937.9 ± 42.4	u.k.	−1762.5 ± 20.0	u.k.
Ho	−1881.0 ± 0.5	−1003.2 ± 5.5	−996.2 ± 7.4	−1948.1 ± 33.2	u.k.	−1774.1 ± 9.5	u.k.
Er	−1898.1 ± 0.6	−996.8 ± 2.6	−993.9 ± 5.5	−1957.0 ± 28.1	u.k.	−1782.5 ± 2.4	u.k.
Tm	−1888.9 ± 0.6	−989.8 ± 4.0	−990.0 ± 1.7	−1946.8 ± 25.4	u.k.	−1777.7 ± 10.4	u.k.
Yb	−1821.7 ± 19.3	−960.3 ± 0.7	−962.2 ± 0.3	−1906.1 ± 33.0	u.k.	−1692.6	u.k.
Lu	−1878.4 ± 0.6	−966.2 ± 23.4	−976.8 ± 22.9	−1948.4 ± 9.9	u.k.	−1789.2	u.k.

u.k. = unknown. [a] Type II oxycarbonates.

whether the ion *i* is monoatomic, linear polyatomic or polyatomic, respectively, and *RT* is approximately 2.5 kJ mol^{-1}.

The thermochemical cycles considered in each BHFC are presented in Fig. S1a–f in ESI.† The values of the lattice enthalpy and the standard enthalpies of sublimation, ionization, dissociation, and electronic affinity used in this work can also be found in the ESI.†

Predictions based on lattice energy calculations using EUGEN

EUGEN is a code for calculating Madelung constants of salts,[58] and outputs Madelung energies ($E_{Madelung}$). Madelung energies output from the EUGEN code were used to estimate lattice potential energies (U_{POT}). Based on the observation of Glasser,[59] lattice potential energies were computed using the relation: $U_{POT} = 0.85E_{Madelung}$. The factor of 0.85 accounts for the fact that Madelung energies are based on coloumbic interactions alone and neglect other types of interactions, such as van der Waals repulsions. Note that, this relation was used to calculate lattice potential energies for all compounds, with the exception of the trichlorides. For the trichlorides it was found that scaling Madelung energies by a factor of 0.85 led to poor corresponding enthalpies of formation, and so for these compounds lattice potential energies were taken to be Madelung energies, without scaling. This is in keeping with the work of Glasser,[59] who reported the Madelung energies and lattice potential energies of $LaCl_3$, and YCl_3 to be within 1–2%. Calculated lattice potential energies were then converted to enthalpies using eqn (3) and input into the BHFC to calculate enthalpies of formation.

The EUGEN code requires the positions and charges of anions and cations in order to calculate Madelung energies. In our calculations compounds were treated as ionic and charges on anions and cations were taken to be their oxidation number. Of course, the validity this is an approximation decreases with the covalent character of the compound, but calculation of the fractional charges on ions is out of the scope of this study. Using the oxidation number means that the method is kept simple and, as we will show, leads to reasonable results.

The crystal structures of the rare earth oxysulfide and sodium lanthanide oxides were taken from The Materials Project (https://materialsproject.org),[60] which contains a database of structures calculated from density functional theory calculations. Due to the absence of some structure for the phosphates, chlorides, and oxychlorides in The Materials Project database, we calculated them ourselves using the density functional theory based VASP code,[61,62] with the projector augmented wave method.[62–64] The PBEsol exchange–correlation functional[65] and an energy cut-off of 1000 eV were used for all calculations. The valence electron configurations for the potentials were: $5s^2\ 5p^6\ 5d^1\ 6s^2$ for all rare earth elements from La to Sm and $5p^6\ 5d^1\ 6s^2$ for all rare earth elements from Eu to La (with the 4f electrons frozen in the core); $3s^2\ 3p^3$ for P; $s^2\ p^5$ for Cl; and $2s^2\ 2p^4$ for O. Brillouin zone sampling was carried out using the following Monkhorst–Pack grids:[66] phosphates (monazite) $4 \times 4 \times 4$; phosphates (xenotime) $4 \times 4 \times 4$; chlorides (hexagonal) $6 \times 6 \times 8$; chlorides (monoclinic) $4 \times 3 \times 4$; oxychlorides $16 \times 16 \times 16$.

In order to validate the use of the EUGEN code for compounds in our test set, we calculated the lattice potential enthalpies for some similar compounds, *e.g.* sulfides, chloride and oxides, for which values determined from experimental data exist.[67] The crystal structures were taken from The Materials Project (https://materialsproject.org)[60] and the charges on ions were taken to be their oxidation number. The results of these calculations are in Table S1 of the ESI.† In general, good agreement is found.

Linear relationship

The correlation between $\Delta H_f^0(Ln_2O_3)$ and ΔH_f^0(LnSalt) for our test set of rare earth compounds is presented in Fig. 1a–c using the values given in Table 1. Promethium was excluded from the analysis due to the lack of data for most of the compounds under study. Moreover, from Table 1 the values for europium and ytterbium compounds are anomalous and so were also excluded from our analysis. Glasser[68] explained that the anomalous behaviour of europium arises from the ground state of Eu^{3+} having zero magnetic spin entropy, compared to other trivalent lanthanide ions, which have finite values. The discrepancy between the enthalpies of formation of Lu and Yb compounds are attributed to a fall in the ionization energy of the ion Lu^{3+} with respect to the Yb^{3+} due to the fully shielded outer f-electron shell of Yb. To our best knowledge, this is the first time these linear relationships have been reported. They offer a new way to predict the enthalpy of formation of rare earth compounds for which values are known for other rare earth elements in the series.

Table 2 shows the statistical descriptors for each regression. As can be observed in Table 2, the r^2 values obtained for $LnCl_3$, Ln_2O_2S and $Ln_2O_2CO_3$ show a linear dependence between $\Delta H_f^0(Ln_2O_3)$ and ΔH_f^0(LnSalt). A poor dependence is observed for LnOCl and $LnPO_4$. However, the *F*-test carried out at a 99% confidence level, shows that F calc $>$ F critical in all cases indicating that there is a relationship between $\Delta H_f^0(Ln_2O_3)$ and ΔH_f^0(LnSalt) in all cases, despite the low r^2 values found for $LnPO_4$ and LnOCl.

Group contribution method

The values of ΔH_f^0(LnSalt) calculated using the group contribution method developed by Mostafa *et al.* are presented in Table S2 (ESI†), where all the values are within 9.0% of available experimental data. Promethium compounds were not calculated because the unknown contribution value for Pm^{3+}. According to the literature review carried out, the type I crystal structure of the oxycarbonates is the most stable at low temperature. However, thermogravimetric studies,[8,69] have confirmed the co-existence of type I and type II oxy-carbonates for the light rare earth elements from 400 to 600 °C as a consequence of their polymorphic nature, which suggests that little difference may exist between the enthalpy of formation of the type I and type II oxy-carbonates.

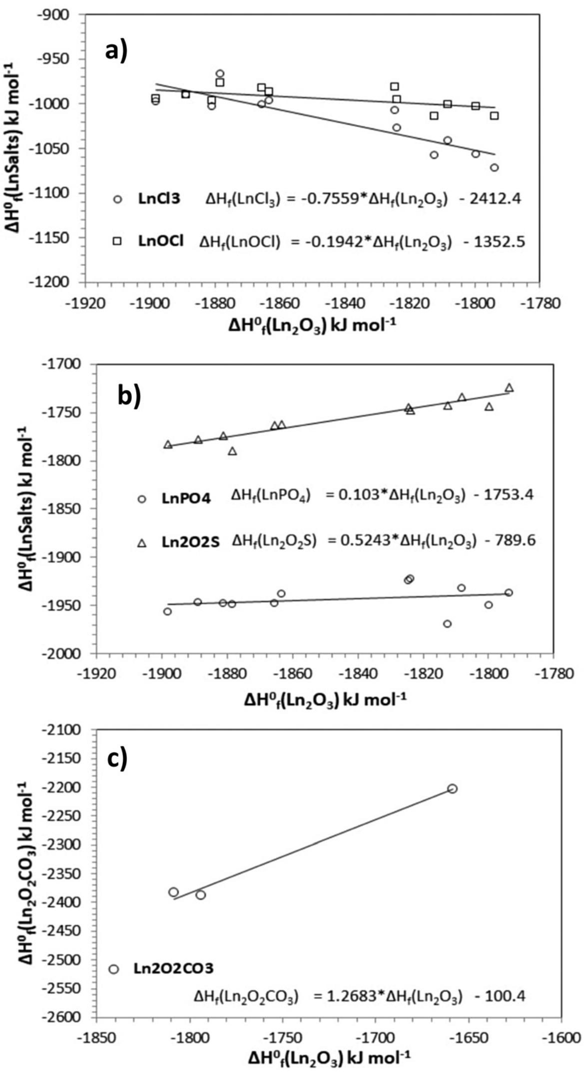

Fig. 1 Relationship between $\Delta H_f^0(Ln_2O_3)$ and ΔH_f^0(LnSalt) for (a) $LnCl_3$ and LnOCl, (b) $LnPO_4$ and Ln_2O_2S and (c) $Ln_2O_2CO_3$. Pm, Eu and Yb were excluded from all analysis and for $Ln_2O_2CO_3$ only La, Nd and Eu were considered.

Table 2 Statistical analysis of the linear regression of lanthanide compounds using experimental values

LnSalt	r^2	*F* calc.	*F* critical
$LnCl_3$	0.7806	35.58	1.38×10^{-4}
LnOCl	0.3768	6.04	3.37×10^{-2}
$LnPO_4$	0.0845	0.92	3.59×10^{-1}
Ln_2O_2S	0.9098	101.81	1.53×10^{-6}
$Ln_2O_2CO_3$	0.9864	72.40	7.44×10^{-2}

No experimental values of the enthalpy of formation were found for the sodium lanthanide oxides. Only Barker *et al.*[70] reported the experimental value of the enthalpy of formation of $NaCeO_2$ as -1127.0 kJ mol^{-1} at 352 °C, which is within reasonable limits of our estimation using Mostafa's *et al.* group contribution method.

Volume based thermodynamics

The VBT method relies on accurate determination of molecular volumes to calculate the lattice energy of solid phases. It is important to bear in mind that propagation of uncertainties of ±10% in the molecular volume can lead to ±20% uncertainties in the calculated enthalpy of formation. In addition, the VBT method assumes ionic character of the compounds studied. The values of the ΔH_f^0(LnSalt) calculated using the volume based thermodynamics are presented in Table S3 (ESI†). As can be observed from Table S3 (ESI†), the average deviation from experimental available data is higher than 14.0%. One of the main reasons for the inaccuracies observed is that the most recent crystal data for the chlorides and oxychlorides are from eighties. In addition, when covalent forces play an important role, eqn (1) and (2) become increasingly unreliable.[3] The oxysalts (LnOCl, $Ln_2O_2CO_3$ and Ln_2O_2S) and the A-Ln_2O_3, can be structurally defined as tri or bi-dimensional packing of OLn_4 tetrahedra sharing edges that appear as an infinite polymeric complex cation $(LnO)_n^{n+}$ which alternate with sheets of the anions. Considering the OLn_4 tetrahedra as the basic structural unit, directional bonding of the oxygen atom might be expected, meaning that a large, but not dominant, covalent contribution may be present in these compounds.[71] Similar structural features may apply to the $NaLnO_2$. However, there is little information available in the literature about them.

EUGEN calculations

To attempt to improve estimations of enthalpies of formation calculated using the BHFC, electrostatic lattice energies determined using the EUGEN code[58] were used as an approximation for lattice potential energies (U_{POT}) in eqn (3). These lead to significantly improved values, except for the phosphates.

Method comparison

In Fig. 2 we present, the absolute error calculated according to eqn (4), for the rare earth chlorides, oxychlorides, oxysulfides and phosphates. When no experimental values were available or the enthalpy of formation could not be predicted by a particular method for some compounds the error was not calculated.

$$\text{Error}(\%) = 100 \times \left|\frac{\Delta H^0_{\text{f exp}} - \Delta H^0_{\text{f calc}}}{\Delta H^0_{\text{f exp}}}\right| \quad (4)$$

Comparison of the methods used with the experimental values for $LnCl_3$, LnOCl, $LnPO_4$ and Ln_2O_2S, indicate that, in general, the group contribution method and the linear relationship provide better values for the enthalpy of formation. Note that, for these four compounds, the linear relationship was calculated by fitting to all the experimental data and so the percentage error simply represents the misfit between the relationship and experimental results, rather than a prediction. In addition, it should be considered that the linear relationship does not give good estimations for Eu and Yb due to their exclusion from the linear analysis. For Ln_2O_2S, the linear relationship predicts values in better agreement with experimental results, due to the contribution of the S^{2-} ion being estimated from the original

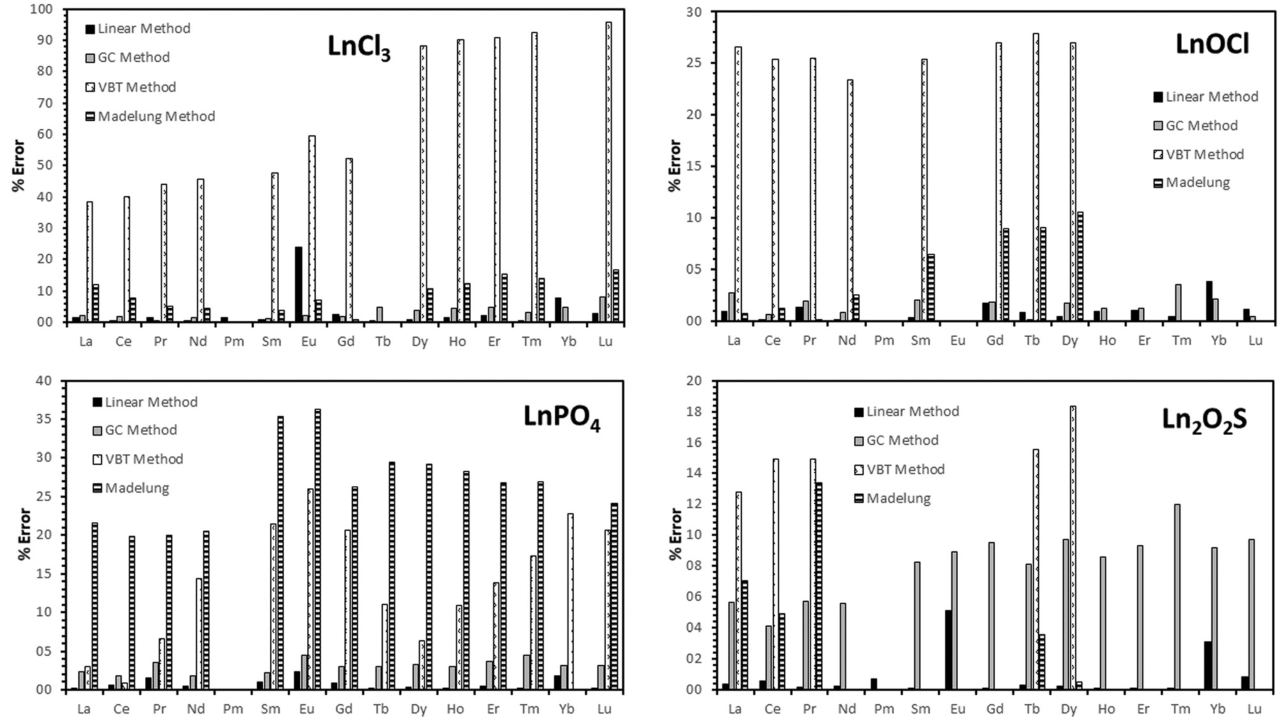

Fig. 2 Comparison between estimated and experimental values of the enthalpy of formation for $LnCl_3$, LnOCl, $LnPO_4$ and Ln_2O_2S.

work of Mostafa *et al.*[1] That said, reasonable estimations were achieved with all estimated values within 12.0% of available experimental data.

The VBT method appears to be unsuitable for estimating the enthalpy of formation of $LnCl_3$ with absolute errors between about 40.0–90.0%. The situation is better for LnOCl and Ln_2O_2S with absolute errors of about 23.0–28.0% and 12.0–19.0% respectively. For $LnPO_4$, the VBT method shows high variability, with absolute errors of between 0.9 to 26%. The correction of the VBT method carried out using EUGEN to calculate U_{POT} rather than eqn (1) and (2) improves the estimations of all the compounds except for $LnPO_4$. These differences are attributed to the values of the parameters A and α, which seem to be unsuitable for lanthanide compounds.

Due to scarce experimental values for $Ln_2O_2CO_3$ and $NaLnO_2$, the group contribution method was taken as a reference for comparison with the other methods, which is presented in Fig. 3. It can be observed that the linear relationship presented in Table 2 for $Ln_2O_2CO_3$ agrees well with the values predicted using the group contribution method, with absolute errors ranging from 0.6–9.0%. This agreement is excellent, considering that the linear relationship was calculated using the enthalpies of formation of just three of the oxycarbonates, and illustrates the predictive power of the method. The VBT method fails in the prediction of the enthalpy of formation of $Ln_2O_2CO_3$, because of the important covalent contribution present. It was not possible to predict values for $Ln_2O_2CO_3$ using the EUGEN code, due to the crystal structure having partial occupancies.

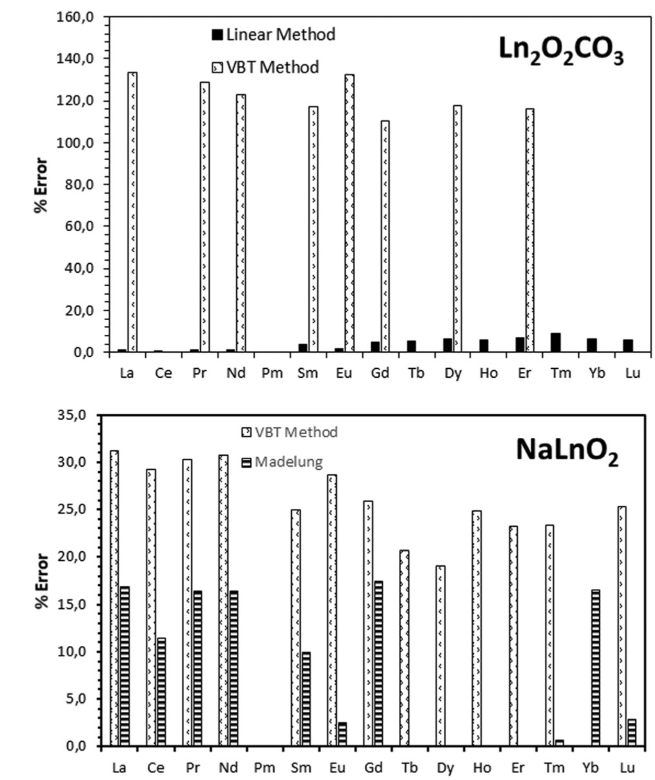

Fig. 3 Comparison between estimated values of the enthalpy of formation with the group contribution, VBT and Madelung methods for $Ln_2O_2CO_3$ and $NaLnO_2$.

For $NaLnO_2$ discrepancies between 19.0–32.0% are reported when the VBT method is used. Better estimations are achieved when for calculations based on lattice potential energies calculated using the EUGEN code, as shown in Fig. 3.

Conclusions

In this work we have compared several methods for calculating the enthalpies of formation of the rare earth compounds: $LnCl_3$, LnOCl, $LnPO_4$, Ln_2O_2S, $Ln_2O_2CO_3$ and $NaLnO_2$. We find that the method of Mostafa *et al.*[1] and our method based on a linear relationship are the most accurate. However, the method of Mostafa *et al.*[1] requires that the contribution of each group is known, while our method based on a linear relationship necessitates that experimental data is available for some of the rare earth compounds. In contrast, the VBT method only requires the molecular volume of a compound, but the accuracy of predicted values is poor when covalent bonding contributions are significant. The calculation of the lattice potential energy using EUGEN instead of eqn (1) and (2) improves the estimation using the BHFC but requires the full crystal structure. This improvement suggests that the value of the parameters α = 139.0 kJ mol^{-1} and A = 123.0 kJ mol^{-1} are unsuitable for the compounds studied. Taken together, these methods provide a complementary suite of techniques for predicting the enthalpies of formation of rare earth compounds, depending on the experimental data available and accuracy desired. Our recommendations are as follows. If enthalpies of formation are available for some rare earth compounds in the series, use the linear relationship. If no enthalpies of formation exist, and all group contributions are available, use the method of Mostafa *et al.*[1] Failing this, use the BHFC. If using the BHFC, and the crystal structure is available, calculating the lattice potential energy using the EUGEN code. If only the volume is available, use the VBT method to calculate the lattice potential energy.

Conflicts of interest

There are no conflicts to declare.

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