



A method for the estimation of the enthalpy of formation of mixed oxides in $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ systems

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ABSTRACT

A new method is proposed for the estimation of the enthalpy of formation ($\Delta_{\text{ox}}H$) of various $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ mixed oxides from the constituent binary oxides. Our method is based on Pauling's concept of electronegativity and, in particular, on the relation between the enthalpy of formation of a binary oxide and the difference between the electronegativities of the oxide-forming element and oxygen. This relation is extended to mixed oxides with a simple formula given for the calculation of $\Delta_{\text{ox}}H$. The parameters of this equation were fitted using published experimental values of $\Delta_{\text{ox}}H$ derived from high-temperature oxide melt solution calorimetry. Using our proposed method, we obtained a standard deviation (σ) of 4.87 kJ mol^{-1} for this data set. Taking into account regularities within the lanthanide series, we then estimated the $\Delta_{\text{ox}}H$ values for $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ mixed oxides. The values estimated using our method were compared with those obtained by Aronson's and Zhuang's empirical methods, both of which give significantly poorer results.

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1. Introduction

Lanthanide aluminate-based ceramics are promising materials, already used in a wide range of optical, magnetic, electronic and structural applications, currently including laser host materials, phosphors, ceramic microwave resonators, scintillators, fuel cells, solid electrolytes, chemical sensors, magnetic refrigeration materials, substrates for high-temperature superconductor deposition, catalyst supports and thermal barrier coatings. To assess the thermodynamic stability and reactivity of these materials under various preparation, processing and operational conditions, a consistent set of thermodynamic properties is required, including heat capacity, entropy, enthalpy of formation and Gibbs energy.

Based on $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ phase diagrams, Wu and Pelton [1] calculated a set of enthalpy ($\Delta_{\text{ox}}H$) and entropy ($\Delta_{\text{ox}}S$) of formation values for various $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ mixed oxides from the constituent binary oxides. While the Gibbs energy data they obtained were consistent with phase equilibria, the enthalpy and entropy terms they derived were not reliable in all cases due to the strong influence of enthalpy–entropy compensation phenomena. Fig. 1 shows the $\Delta_{\text{ox}}H$ values published by various authors for perovskite-type LnAlO_3 oxides. In addition to Wu and Pelton's calculated data, the values derived from various calorimetric measurements [2–6] are also shown. While experimental data

obtained by high-temperature oxide melt solution calorimetry consistently show dependence on the atomic number of the lanthanide elements (Z), Wu and Pelton's $\Delta_{\text{ox}}H$ values are almost independent of Z , falling, with the exception of $\Delta_{\text{ox}}H(\text{LaAlO}_3)$, in the narrow range of -32 to -24 kJ mol^{-1} . As reliable calorimetric values of $\Delta_{\text{ox}}H$ are not available for all $\text{Al}_2\text{O}_3\text{--Ln}_2\text{O}_3$ mixed oxides, it is useful to apply an empirical estimation or correlation method to complete the missing data. Therefore, in this paper, we propose a new empirical method for predicting the enthalpy of formation ($\Delta_{\text{ox}}H$) for various Ln–Al mixed oxides.

2. Methods for estimating the enthalpy of formation of mixed oxides

Various empirical methods have been employed in estimating the enthalpy of formation of mixed oxides from either the elements, $\Delta_f H$, or the constituent binary oxides, $\Delta_{\text{ox}}H$ [7,8]. The simplest, and most general, method is that proposed by Aronson [9]. Aronson's method is based on Pauling's relation between the enthalpy of formation and the differences between the electronegativities of the elements forming the compound. Aronson proposed the following formula for the estimation of $\Delta_f H$ for mixed oxides:

$$\Delta_f H(\text{kJ mol}^{-1}) = -96.5n_{\text{O}}(X' - X_{\text{O}})^2 \quad (1)$$

where n_{O} is the number of oxygen atoms in the formula unit, X_{O} is Pauling's electronegativity of oxygen, and X' is the weighted

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geometrical mean of the so-called “pseudoelectronegativities” of the oxide-forming elements. Pseudoelectronegativity values are derived from known values for the enthalpy of formation of the relevant binary oxides. For Ln_2O_3 oxides, the pseudoelectronegativities X'_{Ln} are calculated as

$$X'_{\text{Ln}} = X_{\text{O}} + \sqrt{\frac{-\Delta_f H(\text{Ln}_2\text{O}_3)}{3 \cdot 96.5}} \quad (2)$$

Table 1 presents the enthalpies of formation $\Delta_f H$ (298.15 K) of lanthanide sesquioxides [10], pseudoelectronegativities (X'_{Ln}) calculated using Eq. (2) and, for comparison purposes, Pauling's electronegativity values (X_{Ln}) [11]. The electronegativities of Pm, Eu, Tb and Yb are not given in [11]. Therefore, based on the fact that electronegativity values slightly increase throughout the lanthanide series [11,12], the values used for Pm, Eu, Tb and Yb were determined by calculating the arithmetic mean of the electronegativities of their adjacent elements; $X_{\text{O}} = 3.44$ [11] was used in all calculations.

Another method, also based on the concept of electronegativity, was proposed by Zhuang et al. [13]. Using this method it is possible to estimate the $\Delta_{\text{ox}}H$ values for binary oxides using the following formula:

$$\Delta_{\text{ox}}H = (n_1 + n_2)x_1x_2\lambda \quad (3)$$

where n_i and x_i are the number of moles and mole fraction, respectively, of the i -th constituent mixed oxide, and λ is a

constant similar to the interaction parameter used in the regular solution model. When $\Delta_{\text{ox}}H$ is known for any double oxide $n_1(A_aO_x) \cdot n_2(B_bO_y)$, the λ parameter can be calculated from the value of $\Delta_{\text{ox}}H$, and then used to calculate the value of $\Delta_{\text{ox}}H$ for double oxides with other stoichiometry. Otherwise, λ can be estimated using the following formula:

$$\lambda = -96.5z(X_A - X_B)^2 \quad (4)$$

where X_A and X_B are Pauling's electronegativities for A and B elements, respectively, and z is a stoichiometric factor given by the relation $z = 2(x/a+y/b)$.

Another group of methods is based on the correlation between the value of $\Delta_{\text{ox}}H$ and the structural parameters of a particular mixed oxide. For example, for perovskite-type double oxides of the general formula ABO_3 , Yokokawa [14] proposed a correlation between $\Delta_{\text{ox}}H$ and the tolerance factor $t = (r_A+r_O)/\sqrt{2(r_B+r_O)}$, where r_A and r_B are the radii of A -site ions with 12-coordination and B -site ions with six-coordination, respectively. This correlation has been successfully applied in the cases of the LnFeO_3 , LnCoO_3 , LnMnO_3 [14], LaBO_3 ($B = \text{Al, Ga, Sc and In}$) [4] and LaMO_3 ($M = \text{Cr, Fe, Co, Ni}$) series [15]. The correlation $\Delta_{\text{ox}}H$ vs. $1/r_{\text{Ln}}$ was proposed and successfully used for the LnAlO_3 , $\text{Ln}_3\text{Al}_5\text{O}_{12}$, LnGaO_3 and $\text{Ln}_3\text{Ga}_5\text{O}_{12}$ [2] series. More recently, this correlation has been used in modified form ($\Delta_{\text{ox}}H$ vs. r_{Ln}) for the $\text{Ln}_2\text{Ti}_2\text{O}_7$, $\text{Ln}_2\text{Zr}_2\text{O}_7$ [16], LnPO_4 and LnVO_4 [17] series.

3. Proposed method

According to Pauling [18], for binary metal oxides (B_bO_y) it holds that

$$\Delta_f H(B_bO_y) = -96.5y(X_B - X_{\text{O}})^2 + 108.8y \quad (5)$$

where X represents electronegativity and y the number of oxygen atoms (O) in the molecule of the oxide under consideration. Therefore, for the basic oxides Ln_2O_3 and Al_2O_3 ($y = 3$) it holds that

$$\begin{aligned} \Delta_f H(\text{Ln}_2\text{O}_3) &= -96.5y(X_{\text{Ln}} - X_{\text{O}})^2 + 108.8y \\ \Delta_f H(\text{Al}_2\text{O}_3) &= -96.5y(X_{\text{Al}} - X_{\text{O}})^2 + 108.8y \end{aligned} \quad (6)$$

Consequently, the natural extension for the mixed oxide $\text{Ln}_a\text{Al}_b\text{O}_y$ takes the following form

$$\begin{aligned} \Delta_f H(\text{Ln}_a\text{Al}_b\text{O}_y) &= -96.5y[x_{\text{Ln}}(X_{\text{Ln}}^* - X_{\text{O}}^*)^2 \\ &\quad + x_{\text{Al}}(X_{\text{Al}}^* - X_{\text{O}}^*)^2] + 108.8y \end{aligned} \quad (7)$$

where $x_{\text{Ln}} = a/(a+b)$ and $x_{\text{Al}} = b/(a+b)$. It holds in our case that the mole fractions of metals are just equal to the mole fractions of metal oxides. The upper index * refers to the electronegativity value of the given element in the $\text{Ln}_a\text{Al}_b\text{O}_y$ double oxide; this value generally differing from Pauling's value due to the fact that the electronegativity of the element changes depending on its actual “chemical environment” (oxidation state of the element and its coordination number) [19]. Since only the differences ($X_{\text{Me}} - X_{\text{O}}$) and ($X_{\text{Me}}^* - X_{\text{O}}^*$) are present in Eqs. (6) and (7), the relation $X_{\text{O}}^* = X_{\text{O}} = 3.44$ [11] is used as a reference state.

According to the reaction



the enthalpy of formation ($\Delta_{\text{ox}}H$) of the mixed oxide $\text{Ln}_a\text{Al}_b\text{O}_y$ from the binary ones is given by the relation

$$\begin{aligned} \Delta_{\text{ox}}H(\text{Ln}_a\text{Al}_b\text{O}_y) &= \Delta_f H(\text{Ln}_a\text{Al}_b\text{O}_y) \\ &\quad - \frac{a}{2}\Delta_f H(\text{Ln}_2\text{O}_3) - \frac{b}{2}\Delta_f H(\text{Al}_2\text{O}_3) \end{aligned} \quad (9)$$

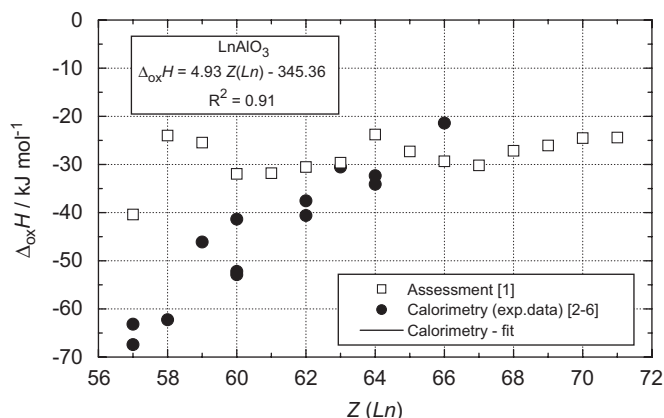


Fig. 1. Enthalpy of formation of LnAlO_3 oxides from the constituent binary oxides.

Table 1

Enthalpies of formation of lanthanide sesquioxides [10], pseudoelectronegativities and Pauling's electronegativities [11] for lanthanide elements.

Ln_2O_3	$\Delta_f H(298.15 \text{ K})$ (kJ mol^{-1})	X'_{Ln}	X_{Ln}
La	-1791.6	0.952	1.10
Ce	-1813.0	0.937	1.12
Pr	-1809.9	0.940	1.13
Nd	-1806.9	0.942	1.14
Pm	-1811.0	0.939	1.155 ^a
Sm	-1826.8	0.928	1.17
Eu	-1662.5	1.044	1.185 ^a
Gd	-1826.9	0.988	1.20
Tb	-1865.2	0.902	1.21 ^a
Dy	-1863.4	0.903	1.22
Ho	-1883.3	0.889	1.23
Er	-1900.1	0.878	1.24
Tm	-1889.3	0.885	1.25
Yb	-1814.5	0.936	1.26 ^a
Lu	-1877.0	0.894	1.27

^a Estimated as the arithmetic mean of adjacent X_{Ln} values.

Substituting Eqs. (6) and (7) into (9), we obtain ($y = 3(a+b)/2$):

$$\Delta_{\text{ox}}H = -96.5y[x_{\text{Ln}}(X_{\text{Ln}}^* - X_{\text{O}})^2 - (X_{\text{Ln}} - X_{\text{O}})^2] + x_{\text{Al}}[(X_{\text{Al}}^* - X_{\text{O}})^2 - (X_{\text{Al}} - X_{\text{O}})^2] \quad (10)$$

Clearly when electronegativity values do not vary (i.e. $X^* = X$), $\Delta_{\text{ox}}H = 0$. Thus, relation (10) can be rewritten in the following form:

$$\Delta_{\text{ox}}H = -96.5y[x_{\text{Ln}}(X_{\text{Ln}}^* - X_{\text{Ln}})(X_{\text{Ln}}^* + X_{\text{Ln}} - 2X_{\text{O}}) + x_{\text{Al}}(X_{\text{Al}}^* - X_{\text{Al}})(X_{\text{Al}}^* + X_{\text{Al}} - 2X_{\text{O}})] \quad (11)$$

It holds that

$$X_{\text{Ln}}^* + X_{\text{Ln}} - 2X_{\text{O}} = X_{\text{Ln}}^* - X_{\text{Ln}} + 2(X_{\text{Ln}} - X_{\text{O}}) \\ X_{\text{Al}}^* + X_{\text{Al}} - 2X_{\text{O}} = X_{\text{Al}}^* - X_{\text{Al}} + 2(X_{\text{Al}} - X_{\text{O}}) \quad (12)$$

Due to the fact that the difference $X^* - X$ is substantially smaller in absolute value than the second term $2(X - X_{\text{O}})$ on the right side of Eq. (12) it is possible to accept the approximation

$$X_{\text{Ln}}^* + X_{\text{Ln}} - 2X_{\text{O}} \approx 2(X_{\text{Ln}} - X_{\text{O}}) \\ X_{\text{Al}}^* + X_{\text{Al}} - 2X_{\text{O}} \approx 2(X_{\text{Al}} - X_{\text{O}}) \quad (13)$$

Inserting (13) into (11), we thus obtain the following formula:

$$\Delta_{\text{ox}}H = -2 \cdot 96.5y[x_{\text{Ln}}(X_{\text{Ln}}^* - X_{\text{Ln}})(X_{\text{Ln}} - X_{\text{O}}) + x_{\text{Al}}(X_{\text{Al}}^* - X_{\text{Al}})(X_{\text{Al}} - X_{\text{O}})] \quad (14)$$

Our preliminary calculations show that a strong correlation exists between the terms $(X_{\text{Ln}}^* - X_{\text{Ln}})$ and $(X_{\text{Al}}^* - X_{\text{Al}})$. Because they are oppositely signed, when one term increases in value, the other decreases, and vice versa. The simplest formula that can be used to describe such a correlation is based on the linear interpolation technique and takes the following form:

$$x_{\text{Ln}}(X_{\text{Ln}}^* - X_{\text{Ln}}) + x_{\text{Al}}(X_{\text{Al}}^* - X_{\text{Al}}) = 0 \quad (15)$$

This formula is clearly valid for the limit values of the mole fractions x_{Ln} , x_{Al} , i.e. when ($x_{\text{Al}} = 0$ and $x_{\text{Ln}} = 1$) or ($x_{\text{Al}} = 1$ and $x_{\text{Ln}} = 0$). It follows from (14) and (15) that

$$\Delta_{\text{ox}}H = -2 \cdot 96.5y x_{\text{Al}}(X_{\text{Al}}^* - X_{\text{Al}})(X_{\text{Al}} - X_{\text{Ln}}) \quad (16)$$

It is reasonable to assume that the absolute value of $(X_{\text{Al}}^* - X_{\text{Al}})$ increases as a function of the mole fraction x_{Ln} (i.e., as the influence of the chemical environment grows), and also as a function of the term¹ $(X_{\text{Al}} - X_{\text{Ln}})$ (the influence of the chemical environment also being dependent on the difference between the electronegativity of Al and that of the relevant lanthanide being considered). Therefore, the following semi-empirical formula is proposed:

$$X_{\text{Al}}^* - X_{\text{Al}} = \alpha x_{\text{Ln}}^\delta (X_{\text{Al}} - X_{\text{Ln}})^\beta, \quad \delta > 0, \beta > 0 \quad (17)$$

Combining (16) and (17), we obtain the final result

$$\Delta_{\text{ox}}H = -2 \cdot 96.5\alpha y x_{\text{Al}} x_{\text{Ln}}^\delta (X_{\text{Al}} - X_{\text{Ln}})^\gamma, \quad \delta > 0, \gamma > 1 \quad (18)$$

where $\gamma = \beta + 1$. This simple estimation formula (18) contains three parameters (α , γ and δ) and is generally valid for any lanthanide–aluminum oxide.

4. Results and discussion

The α , γ and δ parameters of Eq. (18) were fitted using 20 values of $\Delta_{\text{ox}}H$ obtained from calorimetric measurements (Tables 3–5) published in the literature. Some of these values were measured at 298.15 K [3–6], but others were measured at 977 K [2]. To convert the data measured at 977 K to 298.15 K, it is necessary to know the temperature dependencies of the heat

capacities of the relevant Ln–Al oxides (as well as of Ln_2O_3 and Al_2O_3). Unfortunately, dependency data have only been published for NdAlO_3 [20] and GdAlO_3 [21], with the following values having been calculated for the difference $H_{\text{m}}(977) - H_{\text{m}}(298.15)$: $-0.65 \text{ kJ mol}^{-1}$ for NdAlO_3 [20] and 1.69 kJ mol^{-1} for GdAlO_3 [21]. As both values are within the range of uncertainties reported for $\Delta_{\text{ox}}H(977)$, and with no other data available for recalculation, we applied Neumann–Kopp's rule ($\Delta_{\text{ox}}C_{\text{pm}} = 0$) and assumed that $\Delta_{\text{ox}}H(977) = \Delta_{\text{ox}}H(298.15)$.

The fitting procedure we used was a combination of trial-and-error and least-squares optimization. Firstly, various values of γ and δ were chosen. Next, the weights of the individual points $w_i = 1/\sigma_i^2$ were calculated from the uncertainties (σ_i) reported for the $\Delta_{\text{ox}}H$ values. Then, by minimizing the objective function $\Phi(\alpha)$, we calculated the value of α :

$$\Phi(\alpha) = \sum_i w_i (\Delta_{\text{ox}}H_i^{\text{exp}} - \Delta_{\text{ox}}H_i^{\text{calc}})^2 \rightarrow \min, \quad w_i = \frac{1}{\sigma_i^2} \quad (19)$$

Finally, the weighted standard deviation

$$\sigma = \sqrt{\frac{\sum_i w_i (\Delta_{\text{ox}}H_i^{\text{exp}} - \Delta_{\text{ox}}H_i^{\text{calc}})^2}{\sum_i w_i}} \quad (20)$$

was used to measure the goodness of fit. The electronegativity of aluminum, $X_{\text{Al}} = 1.61$ [11], was used in the calculations. The results are summarized in Table 2.

The value of δ influences the point of maximum of the function $x_{\text{Al}}(1 - x_{\text{Al}})^\delta$, $1 - x_{\text{Al}} = x_{\text{Ln}}$. It clearly holds that $x_{\text{Al,max}} = \delta/(1 + \delta)$, i.e. $x_{\text{Al,max}} < 0.5$ when $\delta < 1$, and $x_{\text{Al,max}} > 0.5$ when $\delta > 1$. The value $\delta = 1$ represents the widely used symmetric regular case. In our case, the $x_{\text{Al,max}}$ values were significantly dependent on the value of γ , and the point of maximum fell in both intervals (0;0.5) and (0.5;1). We, therefore, had no reason to prefer the asymmetrical case, and $\delta = 1$ was chosen for further calculations. Under such conditions the lowest value obtained for σ ($\sigma = 4.72$) was achieved when $\gamma = 3.21$. Since there was no statistical difference between the results for $\gamma = 3$ and 3.21, we chose $\gamma = 3$ for further calculations. When $\delta = 1$ and $\gamma = 3$, we obtained $\alpha = 3.307$. All calculated values of $\Delta_{\text{ox}}H$ are summarized in Tables 3–5, and compared with the calorimetric data in Fig. 2. The standard deviation (σ) of 4.87 kJ mol^{-1} obtained using our proposed method represents a very good result, particularly as the quadratic mean of the $\Delta_{\text{ox}}H$ values in the set of calorimetric data is $51.37 \text{ kJ mol}^{-1}$.

We also estimated $\Delta_{\text{ox}}H$ values using the aforementioned methods of Aronson [9] and Zhuang [13]. We used the following pseudoelectronegativity values: X_{Ln} (see Table 1); $X_{\text{Al}} = 1.034$, derived from $\Delta_f H(\text{Al}_2\text{O}_3, 298.15 \text{ K}) = -1675.69 \text{ kJ mol}^{-1}$ [22] and $X_{\text{O}} = 3.44$. Then, the values of $\Delta_f H(\text{Ln}_a\text{Al}_b\text{O}_y)$ were calculated using Eq. (1), and the values of $\Delta_{\text{ox}}H(\text{Ln}_a\text{Al}_b\text{O}_y)$ calculated using Eq. (9) (Tables 3–5). Using Aronson's method, the $\Delta_{\text{ox}}H$ values calculated

Table 2

Standard deviation σ (Eq. (20)) for various combinations of the selected values of γ and δ .

δ	γ								
	2	2.25	2.5	2.75	3	3.25	3.5	3.75	4
0.25	12.11	10.63	9.20	7.85	6.63	5.62	4.92	4.65	4.84 ^a
0.5	10.80	9.36	8.00	6.75	5.69	4.90	4.53 ^a	4.62 ^a	5.13
0.75	9.64	8.27	7.01	5.92	5.07	4.60 ^a	4.58	4.98	5.69
1	8.67	7.41	6.30	5.42	4.87 ^a	4.73	5.01	5.61	6.43
1.25	7.93	6.83	5.93	5.31 ^a	5.06	5.21	5.68	6.39	7.24
1.5	7.46	6.56 ^a	5.90 ^a	5.56	5.57	5.90	6.49	7.24	8.09
1.75	7.29 ^a	6.60	6.19	6.08	6.27	6.71	7.34	8.10	8.93

¹ As $X_{\text{Al}} > X_{\text{Ln}}$ for all lanthanides, the value of $X_{\text{Al}} - X_{\text{Ln}}$ is always positive.

^a Lowest value of σ obtained for given value of γ .

Table 3
Enthalpy of formation of LnAlO₃ oxides from the constituent binary oxides.

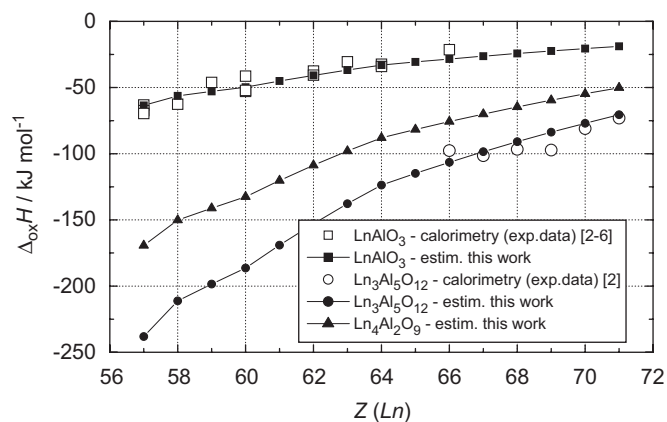
LnAlO ₃	$\Delta_{\text{ox}}H$ (kJ mol ⁻¹)				
	Assessment [1]	Calorimetry [2–6]	Aronson [9]	Zhuang [13]	Our results Eq. (18)
La	-40.38	-63.17 ± 2.52 [2] -69.61 ± 3.23 [4] -67.4 ± 1.5 [6]	-0.71	-37.65	-63.49
Ce	-24.00	-62.55 ± 3.10 [3]	-1.01	-34.75	-56.31
Pr	-25.45	-46.1 ± 1.6 [6]	-0.96	-33.35	-52.93
Nd	-31.94	-41.36 ± 3.44 [2] -52.2 ± 1.4 [5] -52.9 ± 1.7 [6]	-0.92	-31.98	-49.69
Pm	-31.82		-0.98	-29.97	-45.09
Sm	-30.53	-37.55 ± 3.26 [2] -40.6 ± 1.5 [6]	-1.23	-28.02	-40.77
Eu	-29.63	-30.52 ± 2.60 [2]	-0.01	-26.15	-36.74
Gd	-23.79	-32.33 ± 2.96 [2] -34.1 ± 1.7 [6]	-1.23	-24.33	-32.99
Tb	-27.30		-1.98	-23.16	-30.63
Dy	-29.33	-21.39 ± 1.35 [2]	-1.94	-22.02	-28.39
Ho	-30.19		-2.40	-20.90	-26.26
Er	-27.15		-2.83	-19.82	-24.24
Tm	-26.05		-2.55	-18.76	-22.33
Yb	-24.52		-1.03	-17.73	-20.52
Lu	-24.41		-2.25	-16.73	-18.81

Table 4
Enthalpy of formation of Ln₃Al₅O₁₂ oxides from the constituent binary oxides.

Ln ₃ Al ₅ O ₁₂	$\Delta_{\text{ox}}H$ (kJ mol ⁻¹)				
	Assessment [1]	Calorimetry [2]	Aronson [9]	Zhuang [13]	Our results Eq. (18)
La	-108.64		-2.66	-141.19	-238.09
Ce	-70.16		-3.77	-130.33	-211.17
Pr	-81.06		-3.60	-125.06	-198.50
Nd	-125.11		-3.44	-119.91	-186.35
Pm	-132.50		-3.66	-112.38	-169.07
Sm	-138.31		-4.61	-105.09	-152.90
Eu	-158.20		-0.03	-98.05	-137.79
Gd	-147.22		-4.61	-91.25	-123.71
Tb	-173.27		-7.40	-86.85	-114.87
Dy	-190.94	-97.67 ± 3.43	-7.25	-82.56	-106.47
Ho	-203.55	-101.46 ± 10.05	-8.97	-78.38	-98.49
Er	-234.68	-96.66 ± 7.69	-10.58	-74.31	-90.92
Tm	-190.67	-97.20 ± 4.80	-9.53	-70.35	-83.74
Yb	-195.31	-81.03 ± 4.79	-3.86	-66.49	-76.96
Lu	-190.56	-73.08 ± 5.31	-8.41	-62.75	-70.55

Table 5
Enthalpy of formation of Ln₄Al₂O₉ oxides from the constituent binary oxides.

Ln ₄ Al ₂ O ₉	$\Delta_{\text{ox}}H$ (kJ mol ⁻¹)			
	Assessment [1]	Aronson [9]	Zhuang [13]	Our results Eq. (18)
La	-53.02	-1.90	-100.40	-169.31
Ce	-35.61	-2.69	-92.68	-150.16
Pr	-41.28	-2.57	-88.93	-141.16
Nd	-62.78	-2.45	-85.27	-132.52
Pm	-74.38	-2.61	-79.91	-120.23
Sm	-75.57	-3.29	-74.73	-108.73
Eu	-75.81	-0.02	-69.72	-97.98
Gd	-65.01	-3.29	-64.89	-87.97
Tb	-76.07	-5.28	-61.76	-81.69
Dy	-80.06	-5.18	-58.71	-75.71
Ho	-85.50	-6.40	-55.74	-70.04
Er	-79.21	-7.55	-52.84	-64.65
Tm	-84.54	-6.80	-50.03	-59.55
Yb	-81.64	-2.75	-47.29	-54.72
Lu	-84.12	-6.00	-44.62	-50.17

**Fig. 2.** Enthalpy of formation of Ln–Al–O oxides from the constituent binary oxides.

were very low in terms of absolute value and the standard deviation (σ) was $49.81 \text{ kJ mol}^{-1}$. This means that Aronson's method is virtually unusable in the case of $\text{Al}_2\text{O}_3\text{-Ln}_2\text{O}_3$ mixed oxides. This is because the pseudoelectronegativity values for lanthanide elements derived from the enthalpies of formation of Ln_2O_3 are relatively low and almost always the same (see Table 1).

A combination of Zhuang's Eqs. (3) and (4) gives the relation ($z = 6$)

$$\begin{aligned} \Delta_{\text{ox}}H &= -6 \cdot 96.5(X_{\text{Al}} - X_{\text{Ln}})^2(n_{\text{Al}_2\text{O}_3} + n_{\text{Ln}_2\text{O}_3})X_{\text{Al}}X_{\text{Ln}} \\ &= -2 \cdot 96.5yX_{\text{Al}}X_{\text{Ln}}(X_{\text{Al}} - X_{\text{Ln}})^2 \end{aligned} \quad (21)$$

It should be noted that this relation is a special case of our Eq. (18) for $\alpha = 1$, $\gamma = 2$ and $\delta = 1$. The $\Delta_{\text{ox}}H$ values were calculated using $X_{\text{Al}} = 1.61$ [11] and Pauling's electronegativity values (see Table 1). In this case the standard deviation (σ) was $= 18.21 \text{ kJ mol}^{-1}$. Thus, Zhuang's method produced a result that is almost three times better than that obtained using Aronson's method.

It follows from Table 3 (which contains the majority of the calorimetric data) that the interpolation ability of our method is very good and significantly better than other methods. Table 4 only contains calorimetric data for the heavier lanthanide elements (Dy–Lu), which have relatively high electronegativity values (X_{Ln}). It is hard to say whether or not the extrapolation to lower values of X_{Ln} is reliable.

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