Formation Enthalpies of $\text{LaLn}'\text{O}_3$ ($\text{Ln}' = \text{Ho}, \text{Er}, \text{Tm}$ and Yb) Interlanthanide Perovskites

Jianqi Qi^{1,2,3,4}, Xiaofeng Guo¹, Aleksandra Mielewczyk-Gryn^{1,5} and Alexandra Navrotsky^{1,*}

¹ *Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis, CA 95616 USA*

² *College of Physical Science and Technology, Sichuan University, Chengdu, 610064, P. R. China*

³ *Key Laboratory of Radiation Physics and Technology of Ministry of Education, Sichuan University, Chengdu, 610064, P. R. China*

⁴ *Key Laboratory of High Energy Density Physics of Ministry of Education, Sichuan University, Chengdu, 610064, P. R. China*

⁵ *Faculty of Applied Physics and Mathematics, Department of Solid State Physics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland*

* e-mail: anavrotsky@ucdavis.edu

Abstract: High-temperature oxide melt solution calorimetry using $3\text{Na}_2\text{O}\cdot\text{MoO}_3$ at $802\text{ }^\circ\text{C}$ was performed for interlanthanide perovskites $\text{LaLn}'\text{O}_3$ ($\text{Ln}' = \text{Ho, Er, Tm and Yb}$) and lanthanide oxides ($\text{La}_2\text{O}_3, \text{Ho}_2\text{O}_3, \text{Er}_2\text{O}_3, \text{Tm}_2\text{O}_3$ and Yb_2O_3). The enthalpies of formation of these interlanthanide perovskites from binary lanthanide oxides at room temperature ($25\text{ }^\circ\text{C}$) were determined to be $-8.30 \pm 3.40\text{ kJ/mol}$ for LaHoO_3 , $-9.85 \pm 3.04\text{ kJ/mol}$ for LaErO_3 , $-10.80 \pm 2.71\text{ kJ/mol}$ for LaTmO_3 and $-12.33 \pm 2.94\text{ kJ/mol}$ for LaYbO_3 . There is a roughly linear relationships between these enthalpy values and the tolerance factor for these and for other $\text{LaM}^{3+}\text{O}_3$ ($\text{M} = \text{In, Sc, Ga, Al, Fe and Cr}$) perovskites, confirming that the distortion of the perovskites as results from ionic radius difference of A-site and B-site cations, is the main factor determining the stability of these compounds.

Keywords: Perovskite; Lanthanide; Calorimetry; Enthalpy of formation.

Introduction

Mixed metal oxides containing rare earths elements have potential applications in optical devices, batteries, and solid oxide fuel cells [1-3]. Perovskite structure interlanthanide oxide compounds ($\text{LnLn}'\text{O}_3$ with Ln and Ln' representing two different rare earths) are of interest especially as proton conductors, scintillators, and for their unique optical and magnetic properties [2, 4-7]. These compounds were first reported in the 1960s by Schneider [8, 9] and Muller-Budchbaum *et al.* [10, 11]. A comprehensive study of preparation and stability of interlanthanide perovskites was done by Berndt *et al.* [2] and their unique magnetic properties were studied by Kentaro *et al.* [7]. Recently, Artini *et al.* presented a comprehensive study of the preparation and structural properties of interlanthanide perovskite compounds [4, 5, 12]. Bharathy *et al.* [6] reported the growth of single crystals of the interlanthanides series $\text{LaLn}'\text{O}_3$ (Ln'=Y, Ho-Lu) using molten hydroxide fluxes.

Ideal perovskites ABO_3 have cubic structure with space group $Pm\bar{3}m-O_h$ comprised of twelve-coordinated A-sites and six-coordinated B-sites. Specifically, BO_6 octahedra are linked through their corners to form a three-dimensional framework, and the interstices between these octahedra, surrounded by 12 oxygen anions, are occupied by large A cations. The perovskite structure can only be formed if the difference of the ionic radii of constituent elements is big enough that the Goldschmidt tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ is close to unity ($0.7 < t < 1.0$) [13], where r_A , r_B and r_O represent the radius of cation A, cation B and oxygen, respectively [14]. The sum $(r_A + r_O)$ corresponds to the face diagonal of the cell and twice the sum $(r_B + r_O)$ represents the unit cell edge [14]. The cubic perovskite structure only exists with higher t values (0.9 - 1.0), while distorted structures (tetragonal, orthorhombic, or rhombohedral) form if the t value is below 0.9 [13].

Thus, the difference of two lanthanide ion sizes determines whether a mixture of lanthanide oxides crystalizes as a solid solution possessing a rare earth oxide structure or as a

perovskite. Specifically, interlanthanide perovskites (orthorhombic, space group $Pnma$) can only be formed when they are chosen as $Ln = La$, $Ln' = Ho, Er, Tm, Yb$ and Lu ; $Ln = Ce$ and $Ln' = Tm, Yb$ and Lu ; and $Ln = Pr$, $Ln' = Yb$ and Lu [5, 7]. The ionic radius of cation Ln is larger than that of cation Ln' , and a distorted perovskite with Ln occupying the A-site and Ln' the B-site is formed. The distortion increases with decreasing tolerance factor t . The relation of thermodynamics and crystal chemistry is a link between macroscopic thermodynamic (ΔH , ΔS , ΔV) and microscopic structural (bond lengths, tolerance factors, lattice vibrations, electronic structure) properties. Consequently thermodynamic data are of critical importance to evaluate and predict the stability of these perovskite materials. High temperature oxide melt solution calorimetry provides a unique way to evaluate the energetics of perovskite compounds [15]. Several works, focused on the energetic relationship between the formation enthalpies and the structural properties of perovskite compounds, suggested that the tolerance factor is a major determinant of the stability of these compounds [16-18]. Despite these studies in other perovskite systems, energetics of interlanthanide perovskites have not been reported.

In this work, $LaLn'O_3$ ($Ln' = Ho, Er, Tm$ and Yb) interlanthanide perovskite samples were prepared by the high temperature solid-state synthesis, and then characterized by powder X-ray diffraction (XRD) and electron microprobe analysis (EMPA). Enthalpies of formation were derived from experiments conducted by oxide melt drop solution calorimetry. Their energetics were compared with those of other lanthanide perovskites ($LnB'O_3$, $B' = In, Sc, Ga, Al, Cr$ and Fe) to extend the correlation of energetics and tolerance factor.

Experimental Methods

A solid state synthesis method was used to prepare the interlanthanide perovskite samples. La_2O_3 (99.99%, Alfa Aesar), Ho_2O_3 (99.99%, Alfa Aesar), Er_2O_3 (99.9%, Alfa Aesar), Tm_2O_3 (99.9%, Alfa Aesar) and Yb_2O_3 (99.99%, Alfa Aesar) were used as starting materials. Prior to synthesis, all oxides were preheated at 1000 °C in air for 12 hours. Stoichiometric mixtures of starting materials were mixed in an agate mortar, pressed into pellets and calcined in air at 1050 °C (LaHoO_3) and 1450 °C (other samples) for 36 hours. The phase purity of products was determined by XRD using a Bruker-AXS D8 Advance diffractometer (Bruker-AXS inc, Germany) operated at an accelerating voltage of 40 kV and an emission current of 40 mA with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm). Phases were identified using the Jade 6.1 software package (Materials Data Inc, Livermore, CA) equipped with both the International Center of Crystallographic Data (ICCD) Powder Diffraction File (PDF) and the International Center of Structure Data (ICSD). The chemical compositions of the samples were measured by wavelength dispersive spectroscopy (WDS) with a Cameca SX100 instrument (Gennevilliers, France). The measurement was operated at an accelerating voltage of 15 kV, a beam current of 10 nA and a beam size of 1 μm . Before measurements, samples were polished and carbon coated. Lanthanide phosphates were used as standards.

High temperature drop solution calorimetry measurements of interlanthanide compounds and their binary oxides were performed in an AlexSYS isoperibol Tian-Calvet twin calorimeter (Setaram, Cailures, France) operated at 802 °C. The details of the calorimeter and method have been described by Navrotsky [19, 20]. All oxides were annealed at 1000 °C for 12 hours to eliminate any moisture, prior to calorimetry. For each measurement, a ~ 5 mg pellet was loosely pressed, weighed and dropped from room temperature into $3\text{Na}_2\text{O}\cdot\text{MoO}_3$ melt at 802 °C. The calorimeter was calibrated using the heat content of corundum. Oxygen was bubbled through the solvent at 5 ml/min and flushed over it at 50 ml/min.

Results and discussion

Structure and composition of interlanthanide perovskites

X-ray diffraction patterns for all synthesized interlanthanide perovskites can be indexed as orthorhombic perovskite phases. LaErO_3 , LaTmO_3 and LaYbO_3 perovskite begin to crystallize around 700 °C. However to obtain well crystallized samples with sharp X-ray peaks, higher temperature is required and most of the samples in this study were synthesized at 1450 °C. Crystallization of orthorhombic LaHoO_3 was achieved by lowering the calcination temperature to 1050 °C, above which the perovskite transforms to a monoclinic B-type rare earth structure, as previously reported [21]. Our results are consistent with other reports in which the size difference of Ln and Ln' in LnLn'O_3 compounds as represented by the tolerance factor, t , plays a determinative role in the temperature stability range for the perovskite structure [2, 4, 5, 7, 21]. For larger difference of ionic radii (also higher t values), the perovskite phase forms at temperatures as low as 700 °C and persists up to 1800 °C [5], while the compound with lowest t value (e.g., LaHoO_3) shows the perovskite $\rightarrow$ monoclinic B-type structure transition above 1200 °C [21].

The whole pattern fitting refinements show that the lattice parameters increase linearly with increase of ionic radius of the B site cation (Fig. 1), which is consistent with Bharathy's crystallographic data on single crystals of interlanthanides [6]. The unit cell parameters obtained are also consistent with those reported by Martinelli *et al.* [12]. The grain size of all samples is in the micron range as they were calcined at high temperature for a long time. The chemical compositions measured by electron microprobe analysis are listed in Table 1. The results confirm nominal-compositions.

From the structural point of view, the investigated compounds have octahedrally coordinated Ln' elements, with the octahedra significantly distorted and rotated to the same extent along the x and y axes of the pseudo-cubic cell with $a_p \sim a/\sqrt{2}$, $b_p \sim b/\sqrt{2}$ and $c_p \sim c/2$. They are rotated

in opposite directions in adjacent layers in the x and y directions but in the same direction, along the z axis.

The degree of distortion from the cubic perovskite correlates with the Goldschmidt tolerance factor. Even though all interlanthanide compounds in this work have orthorhombic structure, the coordination number of La used for calculating t is 12 (ideal cubic perovskite) instead of 8 (distorted orthorhombic perovskite), since the former represents the distortion from the ideal perovskite. Thus the calculated tolerance factors are between 0.848 (LaHoO₃) and 0.861 (LaYbO₃) (Table 1).

There were earlier controversies concerning the real space group for interlanthanide perovskites. Proposed space groups included polar $Pna2_1$ (for LaYbO₃) [11], $Cmcm$ [22, 23], and $Pnma$ [24]. $Pnma$ was eventually confirmed to be the correct space group [7, 25].

Thermodynamics of interlanthanide perovskites from calorimetric measurements

The enthalpies of drop solution, ΔH_{ds} , of lanthanide oxides (La₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃) and perovskite samples are shown in Table 2. These values equal the sum of the heat content and the solution enthalpy of the sample in the molten solvent, and they increase with increase of ionic radius of cations. The enthalpies of drop solution at 702 °C [26] show an almost linear correlation with r^{-1} of lanthanides, but with some scatter. This trend is confirmed in the present study as a strong linear dependence of ΔH_{ds} on r^{-1} : $\Delta H_{ds} = (7.5 \pm 0.4) \times 10^2 \cdot r^{-1} - (9.4 \pm 0.4) \times 10^2$ (kJ/mol) ($R^2 = 0.989$) (shown in Fig. 2). The stronger correlation in the present work may be due to the careful annealing and handling of these hygroscopic rare-earth oxides prior to calorimetry.

The values of drop solution enthalpies of perovskites and binary rare earth oxides were used in thermochemical cycles (Table 3) to derive the enthalpies of formation of interlanthanide perovskites from their binary oxides at 25 °C ($\Delta H_{f,ox}$), shown in Table 2. $\Delta H_{f,ox}$ were plotted

against reciprocal ionic radius of Ln^{3+} , r^{-1} in Fig. 3, and against the tolerance factor t in Fig. 4. $\Delta H_{f,ox}$ of interlanthanide perovskites are close to zero, suggesting the low stability of these compounds. This is consistent with the conclusion obtained from structural point of view that their tolerance factors much less than unity due to the large distortion from the ideal cubic perovskite structure [16-18, 27].

Relationship between structure and stability

The results obtained in the current work can be compared with data for $\text{LaM}^{3+}\text{O}_3$ perovskites ($M = \text{In, Sc, Ga, Al, Cr and Fe}$) from Cheng *et al.* [16, 17] and Kanke *et al.* [18]. A linear correlation was found between $\Delta H_{f,ox}$ and structure, following the equation:

$$\Delta H_{f,ox} = - (0.9 \pm 0.1) \times 10^2 \cdot r^{-1} + (0.9 \pm 0.2) \times 10^2 \text{ (kJ/mol)}, R^2 = 0.892, \quad (1)$$

In the interlanthanide perovskite region, the ionic radii of B cation is large and thus higher order terms in r^{-1} can be neglected, leading to a linear relationship between $\Delta H_{f,ox}$ and r^{-1} , with $R^2 = 0.892$. This relation implies that the energy landscape of $\text{LaLn}'\text{O}_3$ is mainly a matter of Coulomb energy of the interaction between Ln' in the B site and its coordinated oxygen.

The other way to estimate the stability of perovskite is by linking $\Delta H_{f,ox}$ and the tolerance factor t . That approach was widely used for various kinds of perovskites with different cations in the B site, and a linear relationship was found previously [16, 17]. For instance, having the A site cation unchanged, $\Delta H_{f,ox}$ of BaMO_3 perovskites ($M = \text{Ce, Pr}$) [28], and LaMO_3 ($M = \text{In, Sc, Ga, Al, Cr and Fe}$) [16-18] show linear trends against t . As t increases, $\Delta H_{f,ox}$ becomes more exothermic. Here we combine our data with work done by Cheng *et al.* [16, 17] and Kanke *et al.* [18], and they show that previously found linear relationship is maintained, giving:

$$\Delta H_{f,ox} = - (4.3 \pm 0.4) \times 10^2 \cdot t + (3.6 \pm 0.4) \times 10^2 \text{ (kJ/mol)}, R^2 = 0.924, \quad (2)$$

Enthalpies of formation from oxides of perovskite phases become more exothermic, thus the stability of these phases increases as the tolerance factor t increases toward unity. Including the interlanthanide perovskites significantly increases the range of both tolerance factor and enthalpy of formation over which this relationship holds. The results also are consistent with other reports of the stability of LaMO_3 , obtained by thermogravimetry or the electromotive force method [29, 30]. The relation does not change with the degree of distortion and a single trend holds for cubic, orthorhombic and trigonal perovskites. Similar trends for the stability of perovskites also can be found for $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ or $\text{A}^{1+}\text{B}^{5+}\text{O}_3$ perovskites with different space groups [16, 18, 27, 31].

In $\text{LaLn}'\text{O}_3$, as size of cation in the B site increases, the distortion of the Ln'^{3+} coordination octahedron becomes larger, as does the degree of distortion of the structure from cubic symmetry. These factors destabilize the perovskite. The data suggest that at a maximum ionic radius of cation in the B site of 0.96 to 0.98 Å, $\Delta H_{f,ox}$ becomes equal to zero, placing a limit on the existence of interlanthanide perovskites and explaining why no $\text{LaLn}'\text{O}_3$ perovskite phase forms for $\text{Ln}' = \text{Ce}, \text{Pr}, \text{or Nd}$.

Conclusion

High-temperature oxide melt solution calorimetry was performed on four interlanthanide perovskite compounds $\text{LaLn}'\text{O}_3$ ($\text{Ln}' = \text{Ho, Er, Tm and Yb}$) and their enthalpies of formation from binary oxides were obtained. These interlanthanide perovskites follow the same linear relationship between the energetic stability and tolerance factor t as other more stable perovskites containing lanthanide in the A-site and elements such as Al, Fe, and Ga in the B-site.

Acknowledgements

This work was supported by the U.S. Department of Energy. Office of Basic Energy Sciences, grant DEFG0203ER46053.

Reference

- [1] G.-y. Adachi, N. Imanaka, *Chemical reviews* 98 (1998) 1479-1514.
- [2] U. Berndt, D. Maier, C. Keller, *Journal of Solid State Chemistry* 13 (1975) 131-135.
- [3] C. Peng, Z. Zhang, *Ceramics international* 33 (2007) 1133-1136.
- [4] C. Artini, G. Costa, R. Masini, *Journal of thermal analysis and calorimetry* 103 (2011) 17-21.
- [5] C. Artini, G.A. Costa, M.M. Carnasciali, R. Masini, *Journal of Alloys and Compounds* 494 (2010) 336-339.
- [6] M. Bharathy, A.H. Fox, S.J. Mugavero, H.C. zur Loye, *Solid State Sciences* 11 (2009) 651-654.
- [7] K. Ito, K. Tezuka, Y. Hinatsu, *Journal of Solid State Chemistry* 157 (2001) 173-179.
- [8] S. Schneider, R. Roth, *J. Research Natl. Bur. Standards* 64 (1960).
- [9] S. Schneider, R. Roth, *Journal of the American Ceramic Society* 43 (1960) 115-115.
- [10] H. Müller - Buschbaum, C. Teske, *Zeitschrift für anorganische und allgemeine Chemie* 369 (1969) 249-254.
- [11] H. Müller - Buschbaum, C. Teske, *Zeitschrift für anorganische und allgemeine Chemie* 369 (1969) 255-264.
- [12] A. Martinelli, R. Masini, C. Artini, G.A. Costa, L. Keller, *Journal of Physics: Condensed Matter* 25 (2013) 426005.
- [13] W.R. Moser, J. Happel, *Catalytic chemistry of solid-state inorganics*. New York Academy of Sciences New York, 1976.
- [14] V.M. Goldschmidt, *Naturwissenschaften* 14 (1926) 477-485.
- [15] A. Navrotsky, *Chemistry of materials* 10 (1998) 2787-2793.
- [16] J. Cheng, A. Navrotsky, *Journal of materials research* 18 (2003) 2501-2508.
- [17] J. Cheng, A. Navrotsky, X.-D. Zhou, H.U. Anderson, *Journal of materials research* 20 (2005) 191-200.
- [18] Y. Kanke, A. Navrotsky, *Journal of Solid State Chemistry* 141 (1998) 424-436.
- [19] A. Navrotsky, *Physics and Chemistry of Minerals* 2 (1977) 89-104.
- [20] A. Navrotsky, *Physics and Chemistry of Minerals* 24 (1997) 222-241.
- [21] N. Okita, A. Higashide, M. Saito, H. Yamamura, *Procedia Engineering* 36 (2012) 2-6.
- [22] E. Ruiz-Trejo, M.S. Islam, J.A. Kilner, *Solid State Ionics* 123 (1999) 121-129.
- [23] R.L. Moreira, A. Feteira, A. Dias, *Journal of Physics: Condensed Matter* 17 (2005) 2775.
- [24] J. Moreau, *MATERIALS RESEARCH BULLETIN* 3 (1968) 427.
- [25] A. Feteira, L.J. Gillie, R. Elsebrock, D.C. Sinclair, *Journal of the American Ceramic Society* 90 (2007) 1475-1482.
- [26] S. Ushakov, K. Helean, A. Navrotsky, L. Boatner, *Journal of materials research* 16 (2001) 2623-2633.
- [27] E. Takayama-Muromachi, A. Navrotsky, *Journal of Solid State Chemistry* 72 (1988) 244-256.
- [28] S. Ushakov, J. Cheng, A. Navrotsky, J. Wu, S. Haile, *MRS Proceedings*, Cambridge Univ Press, 2002, pp. D7. 17.
- [29] T. Nakamura, G. Petzow, L.J. Gauckler, *MATERIALS RESEARCH BULLETIN* 14 (1979) 649-659.
- [30] O.M. Sreedharan, M.S. Chandrasekharaiah, *Journal of Materials Science* 21 (1986) 2581-2584.

- [31] C. Laberty, A. Navrotsky, C.N.R. Rao, P. Alphonse, *Journal of Solid State Chemistry* 145 (1999) 77-87.
- [32] R.D. Shannon, *Acta Crystallographica Section A* 32 (1976) 751-767.
- [33] A. Mielewczyk-Gryn, S. Wachowski, K.I. Lilova, X. Guo, M. Gazda, A. Navrotsky, *Ceramics International* 41 (2015) 2128-2133.
- [34] R.A. Robie, B.S. Hemingway, *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar pressure and at higher temperatures*. 1995.

Table 1 Sample characterization for (LaLn'O₃, Ln' = Ho, Er, Tm and Yb) interlanthanide perovskite samples with orthorhombic symmetry, space group *Pnma*.

Perovskite	Composition [*]		Lattice parameters [‡]			Tolerance factor
	La site	Ln' site	<i>a</i>	<i>b</i>	<i>c</i>	
LaHoO ₃	1.00(3)	1.01(2)	6.094(2)	8.498(4)	5.881(2)	0.8482 [§]
LaErO ₃	1.02(3)	0.98(1)	6.078(4)	8.466(5)	5.868(4)	0.8522
LaTmO ₃	1.03(3)	0.98(2)	6.056(8)	8.436(1)	5.857(7)	0.8560
LaYbO ₃	1.02(3)	0.98(2)	6.035(3)	8.410(4)	5.835(3)	0.8605

^{*} Calculated based on the microprobe results from 10 points data for each sample. [‡] Calculated from XRD WPF refinement. [§] Calculated from Shannon's database of ionic radii [32].

Table 2

The enthalpies of drop solution of constituent binary oxides of interlanthanide perovskites in 3Na₂O·4MoO₃ at 802°C, and the enthalpies of formation of perovskites at 25 °C.

RE oxides	$\Delta H_{ds}(\text{kJ/mol})$	perovskites	$\Delta H_{ds}(\text{kJ/mol})$	$\Delta H_{f,ox}(\text{kJ/mol})$	$\Delta H_f^\circ(\text{kJ/mol})^\S$
La ₂ O ₃	-221.81 [*] ± 2.25 [†] (7) [‡] [33]				
Ho ₂ O ₃	-109.51 ± 1.50 (6)	LaHoO ₃	-157.08 ± 2.07 (8)	-8.3 ± 3.4	-1845.8 ± 8.0
Er ₂ O ₃	-107.20 ± 1.42 (6)	LaErO ₃	-155.97 ± 1.45 (6)	-9.9 ± 3.0	-1855.8 ± 6.9
Tm ₂ O ₃	-97.97 ± 0.93 (6)	LaTmO ₃	-150.64 ± 1.14 (6)	-10.8 ± 2.7	-1851.3 ± 6.2
Yb ₂ O ₃	-82.65 ± 1.06 (6)	LaYbO ₃	-141.22 ± 1.55 (6)	-12.3 ± 2.9	-1815.4 ± 6.5

^{*} Average. [†] Two standard deviations of the average value. [‡] Number of measurements. [§] values calculated using the values of enthalpy of formation of binary oxides and reference data[34].

Table 3 Thermochemical cycles for determination of the enthalpies of formation of $\text{LaLn}'\text{O}_3$ perovskite from binary oxides at 25 °C.

Reaction	ΔH
(1) $\text{La}_x\text{Ln}'_{2-x}\text{O}_{3(\text{s}, 25\text{ °C})} \rightarrow x/2 \text{La}_2\text{O}_{3(\text{sln}, 802\text{ °C})} + (2-x)/2 \text{Ln}'_2\text{O}_{3(\text{sln}, 802\text{ °C})}$	ΔH_1
(2) $\text{La}_2\text{O}_{3(\text{s}, 25\text{ °C})} \rightarrow \text{La}_2\text{O}_{3(\text{sln}, 802\text{ °C})}$	ΔH_2
(3) $\text{Ln}'_2\text{O}_{3(\text{s}, 25\text{ °C})} \rightarrow \text{Ln}'_2\text{O}_{3(\text{sln}, 802\text{ °C})}$	ΔH_3
$x/2 \text{La}_2\text{O}_{3(\text{s}, 25\text{ °C})} + (2-x)/2 \text{Ln}'_2\text{O}_{3(\text{s}, 25\text{ °C})} \rightarrow \text{La}_x\text{Ln}'_{2-x}\text{O}_{3(\text{s}, 25\text{ °C})}$	
$\Delta H_{\text{f,ox}} = -\Delta H_1 + x/2\Delta H_2 + (2-x)/2\Delta H_3$	$\Delta H_4 = \Delta H_{\text{f,ox}}$

Fig. 1 Lattice parameters obtained from whole profile fitting procedure versus ionic radius of Ln' in LaLn'O₃ perovskites. The lattice parameters increase linearly against the ionic radius of B site cation, R^2 for parameter a (square), b (diamond), and c (circle), are 0.993, 0.998, and 0.991, respectively.

Fig. 2 Drop solution enthalpy of Ln₂O₃ as function of reciprocal ionic radius of Ln³⁺, r^{-1} .

Fig. 3 Enthalpies of formation of LaMO₃ as function of reciprocal ionic radius of M³⁺, r^{-1} .

Fig. 4 Enthalpies of formation of LaMO₃ as function of tolerance factor, t .

Figure %

Figure 8

Figure'

Figure'

A linear relationship between the enthalpy of formation and the tolerance factor for interlanthanide $\text{LaLn}'\text{O}_3$ ($\text{Ln}' = \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$) and other $\text{LaM}^{3+}\text{O}_3$ ($\text{M} = \text{In}, \text{Sc}, \text{Ga}, \text{Al}, \text{Fe}$ and Cr) perovskites.